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INORGANIC AND ORGANIC CHEMISTRY

REACTIONS BETWEEN Ce_2O_3 AND SiO_2 AT HIGH TEMPERATURES

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It has been shown by experiments that chemical compounds are not formed when CeO_2 and SiO_2 react with each other. However, oxides of trivalent rare-earth elements form silicates with silica. Toropov and Bondar' [1] investigated the system $La_2O_3 - SiO_2$, in which three chemical compounds are formed: $La_2O_3 \cdot SiO_2$, $2La_2O_3 \cdot 3SiO_2$, and $La_2O_3 \cdot 2SiO_2$. On the other hand, in a brief report by Warshaw and Roy [2] on an investigation of rare-earth silicates, the authors indicate the formation of two types of chemical compounds: $Ln_2O_3 \cdot SiO_2$ and $Ln_2O_3 \cdot 2SiO_2$ in a number of $Ln_2O_3 - SiO_2$ systems (Ln = La, Nd, Gd, Dy, Eu, Yb, Y).

TABLE 1. Crystalline Structures of Lanthanum Silicates [3]

Molar ratio	0,55	0,76	1,09	1,31	1,53	1,75	1,97	2,18	2,40	2,72
SiO_2/La_2O_3 Structure*	A	A	B	B	B+C	C	C	C	C	C

*A represents La_4SiO_8, B – La_2SiO_5 and C – $La_2Si_2O_7$.

Wanmaker, de Graaf and Spier [3] synthesized the compound $2La_2O_3 \cdot SiO_2$ and investigated it by means of x-rays. Together with the principal components La_2O_3 and SiO_2, 10 mole % of LaF_3 was added to the mixture, the authors believing that this would assist more intense formation of the compounds. The mixtures were roasted in air at 1200°. The crystalline structures of lanthanum silicates were obtained (see Table 1).

In experiments where LaF_3 was not added to the mixture, structure A was obtained at molecular compositions SiO_2/La_2O_3 from 0.5 to 1.2, while structure B was obtained from 1.2 to 2.5.

The present communication gives the results of an investigation of the reaction in the system $Ce_2O_3 - SiO_2$. In view of the fact that Ce_2O_3 is unstable in air, silicates of trivalent cerium were synthesized in a reducing gaseous medium.

EXPERIMENTAL

Cerium dioxide (CeO_2 99.1%, R_2O_3 0.1, other matter 1%) and silica of A. R. Grade served as the initial materials for the charge. The experimental procedure was developed for cerium oxides. When cerium dioxide was heated in an atmosphere of hydrogen, the oxide was reduced according to the reaction: $2CeO_2 + H_2 = Ce_2O_3 + H_2O$. The degree of reduction of cerium dioxide was determined by weighing a sample on a torsion balance. With complete reduction of CeO_2 to Ce_2O_3 the loss in weight was 4.645%, which for a 500-mg sample of CeO_2 was 23.22 mg. Pure Ce_2O_3 was obtained in dry air at 1300° (Fig. 1).

When mixtures of cerium dioxide and silica were heated in hydrogen, Ce_2O_3, which also reacted with the silica, was formed. Mixtures with a $Ce_2O_3:SiO_2$ molecular ratio of 2:1, 1:1, 2:3, 1:2, 1:4, and 1:8 were investigated. The cerium silicates were synthesized in the 1200-1650° range.

The reaction products obtained by roasting in a reducing atmosphere were subjected to gravimetric oxidizing analysis. This analysis is based on the fact that cerium silicates of different composition do not have the same resistance to oxidation by oxygen, and decompose at different temperatures when heated in air. The analytical procedure is described in detail below.

The x-ray investigation of cerium silicates was carried out in an apparatus with ionization recording of the x-rays. A finely ground sample was pressed in a Plexiglas boat. For photographs at high temperatures the sample was pressed in a platinum holder. Filtered KdCu radiation was used. X-ray data on Ce_2O_3 and SiO_2 from the ASTM card index [4] were used as standards of the known (initial) phases when the phase analysis was carried out. The x-ray diffraction pattern of Ce_2O_3 was calculated from the parameters given in a monograph by Ormont [5]: hexagonal lattice α 3.88 kX; c 6.60 kX, oth. gr. $D^3_{3d} - C\bar{3}m$. Intensities were assigned to the x-ray lines with reference to the x-ray diffraction pattern of La_2O_3.

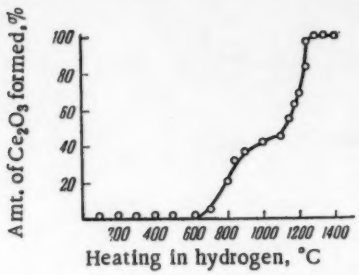

Fig. 1. Formation of Ce_2O_3 from CeO_2 in an atmosphere of hydrogen.

The refractive indices of crystals of the synthesized substances were measured with a microscope; phosphoric immersion liquids with refractive indices from 1.78 to 2.04 were used. The specific gravities of the materials obtained were determined pyknometrically (in kerosene). The electrical properties (dielectric permeability and dielectric losses) of the materials were measured by I. S. Yanchevskaya.

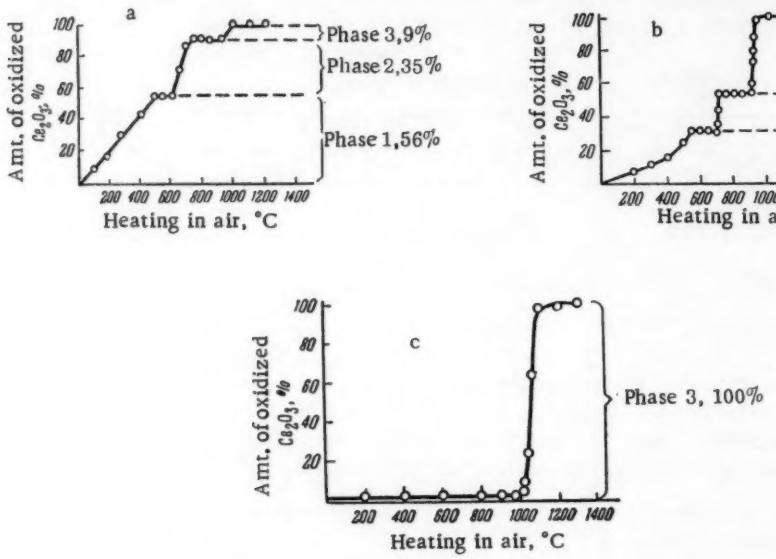

Fig. 2. Gravimetric oxidizing analysis of products in a $1Ce_2O_3 + 2SiO_2$ mixture after heating in hydrogen at 1250° and the following residence times: a) 2 hr; b) 26 hr; c) 32 hr.

Investigation of the Mixtures $1Ce_2O_3 + 2SiO_2$, $1Ce_2O_3 + 4SiO_2$, and $1Ce_2O_3 + 8SiO_2$

A mixture with the composition $1Ce_2O_3 + 2SiO_2$ was roasted at 1250°, retained in hydrogen for 2 hr, and then subjected to gravimetric oxidizing analysis. The analytical results are given in Fig. 2a. The points on the graph showing the weight variation of the sample were obtained by keeping the sample at the temperatures indicated on the abscissa until the weight was constant. As was shown by the investigations, phases differing in resistance to oxidation in air were formed in the mixture. The first phase (56% calculated with respect to Ce_2O_3) was oxidized in the room temperature to 500° range, with formation of free cerium dioxide and silica. The second phase (35%) was oxidized and decomposed into the initial oxides in the 600-700° range, and the third phase (9%) was oxidized above 900°. After three roastings in hydrogen at 1250° with intermediate grinding of the mixture and a total residence time of 26 hr, the product contained 31% of the first phase, 22% of the second, and 47% of the third (Fig. 2b). After six roastings with intermediate grinding in a mortar and a total residence time of 32 hr, all the Ce_2O_3 was combined in the form of a homogeneous phase, oxidized above 900°, as shown in Fig. 2c. The final compound obtained corresponds to the composition $Ce_2O_3 \cdot 2SiO_2$. In the investigated mixture the first and second phases are intermediate.

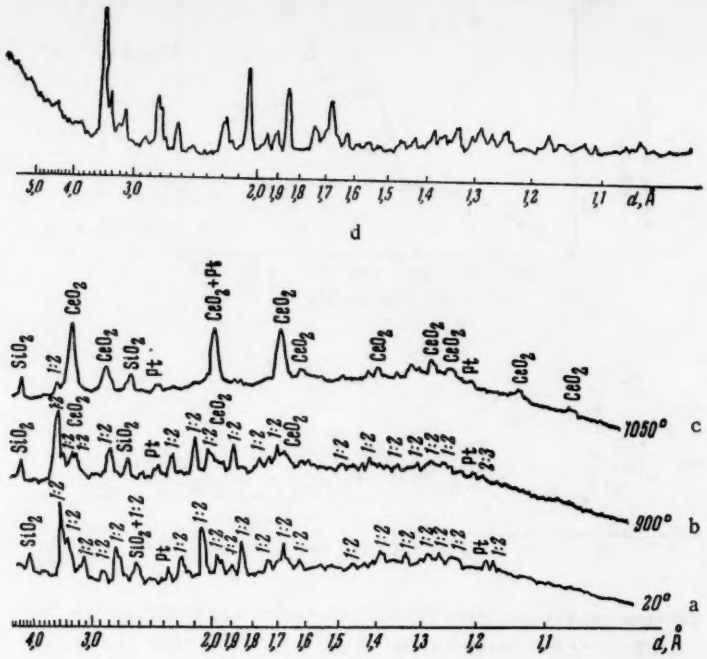

Fig. 3. X-ray diffraction patterns of the products in $Ce_2O_3 + 4SiO_2$ (a,b,c), and $Ce_2O_3 + 2SiO_2$ (d) mixtures after heating in hydrogen.

TABLE 2. X-ray Diffraction Patterns of the Compound $Ce_2O_3 \cdot 2SiO_2$

I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å	I	d, Å
8	4,35	34	2,67	65	2,035	4	1,573	12	1,294	8	1,117
8	3,77	9,6	2,62	6	1,97	7	1,545	19	1,280	8	1,103
100	3,40	24	2,51	15	1,935	11	1,520	12	1,260	4	1,080
38	3,26	6	2,40	16	1,883	10	1,457	15diff.	1,24—1,23	6	1,067
17	3,17	1	2,30—2,25	48	1,834	10	1,422	4	1,203	3	1,060
25	3,08	21	2,18	18	1,725	4	1,403	6	1,183	10	1,050
5	3,00	27	2,15	15	1,70—1,68	13	1,377	13	1,167	4	1,039
8	2,84	8	2,12	37	1,666	8	1,358	8	1,148	3	1,020
40	2,70	4	2,08	13	1,611	19	1,326	4	1,127		

With an excess of silica, for example in a $Ce_2O_3 + 4SiO_2$ mixture, the formation of $Ce_2O_3 \cdot 2SiO_2$ is more marked. With an increase in the roasting temperature the intensity of formation of this compound increased markedly. At 1650° and a residence time of 1 hr, the components in a $1Ce_2O_3 + 2SiO_2$ mixture were completely combined into the compound $Ce_2O_3 \cdot 2SiO_2$.

Like the results of the gravimetric oxidizing analysis of the product containing 31% of the first phase, 22% of the second, and 47% of the third (see Fig. 2b), x-ray analysis showed the presence of three compounds in this product.

With an increase in the silica content in the mixtures, for example with the initial compositions $1Ce_2O_3 + 4SiO_2$ and $1Ce_2O_3 + 8SiO_2$, the chemical compound $Ce_2O_3 \cdot 2SiO_2$ was formed by roasting in hydrogen, and the excess silica was present in the form of cristobalite, as may be seen from Fig. 3a. X-ray analysis at elevated temperatures completely confirmed the gravimetric analysis data with respect to the stability of the compound $Ce_2O_3 \cdot 2SiO_2$. From an examination of the x-ray diffraction patterns (Fig. 3b and 3c) it may be seen that the compound $Ce_2O_3 \cdot 2SiO_2$ prevails up to 900° when heated in air, and decomposes completely at 1050°. The x-ray diffraction pattern of $Ce_2O_3 \cdot 2SiO_2$ is given in Fig. 3d and in Table 2.

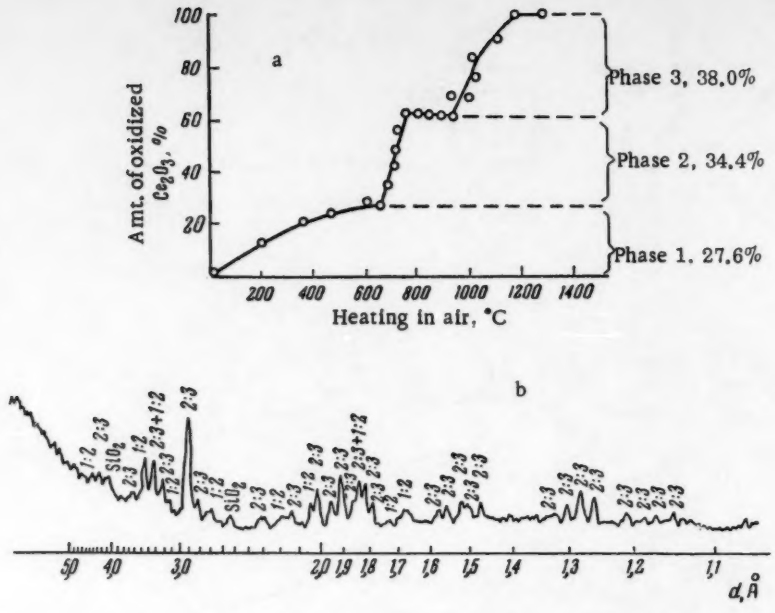

Fig. 4. Gravimetric (a) and x-ray (b) analysis of products in a $2Ce_2O_3 + 3SiO_2$ mixture after heating in hydrogen at 1650° and a residence time of 8 hr.

From these experiments it is evident that in $1Ce_2O_3 + 2SiO_2$ mixtures, and in mixtures with a high silica content, one stable compound with the composition $Ce_2O_2 \cdot 2SiO_2$ is formed in the investigated temperature range of 1250-1650°. The mean refractive index of $Ce_2O_3 \cdot 2SiO_2$ crystals is 1.77, the birefringence is 0.015, and the specific gravity is 4.93. The dielectric permeability and the dielectric-loss angle of material with the composition $Ce_2O_3 \cdot 2SiO_2$ were determined (Table 3).

TABLE 3. Electrical Characteristics of $Ce_2O_3 \cdot 2SiO_2$* (Sample Roasted at 1550° with Residence Time of 4 hr)

Temp., °C	f, cps	tan δ	ε
Room	$1 \cdot 10^3$	$8 \cdot 10^{-3}$	4,85
»	$1 \cdot 10^5$	$4 \cdot 10^{-3}$	4,3
»	$5 \cdot 10^5$	$3 \cdot 10^{-3}$	3,9
100	$1 \cdot 10^5$	$9{,}4 \cdot 10^{-3}$	5,3
100	$5 \cdot 10^5$	$8{,}2 \cdot 10^{-3}$	5,1

*The compound $Ce_2O_3 \cdot 2SiO_2$ melts at 1760° (in hydrogen).

Investigation of a $2Ce_2O_3 + 3SiO_2$ Mixture

Gravimetric oxidizing analysis showed the presence of three phases in a $2Ce_2O_3 + 3SiO_2$ mixture, roasted at 1250° and retained for 6 hr: 42% of the first phase, 33% of the second, and 25% of the third. The composition of the reaction products was unchanged by longer residence times at this temperature. At a synthesis temperature of 1650°, the quantitative ratio of the phases was different: 27.6% of the first phase, 34.4% of the second, and 38.0% of the third (Fig. 4a). As was indicated above, $Ce_2O_3 \cdot 2SiO_2$ oxidizes in air above 900° (third phase). By analogy with lanthanum silicates [1] it was assumed that the second phase is the compound $2Ce_2O_3 \cdot 3SiO_2$ and the first phase is $Ce_2O_3 \cdot SiO_2$. As a result of the ease with which free Ce_2O_3 and Ce_2O_3, combined into the compound $2Ce_2O_3 \cdot SiO_2$, are oxidized in air (room temperature to 500° range), the quantitative determination of these phases by gravimetric oxidizing analysis was difficult.

X-ray analysis showed that three phases: $2Ce_2O_3 \cdot 3SiO_2$, SiO_2, and Ce_2O_3 and CeO_2 are present in samples with the composition $2Ce_2O_3 + 3SiO_2$ in the case of low (1250°) synthesis temperatures. At higher synthesis temperatures (1300-1650°) the silicate $Ce_2O_3 \cdot 2SiO_2$ appears in the samples. It should be noted that Ce_2O_3 (or CeO_2), which must have been present in excess if $Ce_2O_3 \cdot 2SiO_2$ were formed in these samples, did not appear – or only very weakly – in the x-ray diffraction patterns. Nor was the silicate $Ce_2O_3 \cdot SiO_2$ detected in the samples by x-ray analysis. The characteristic x-ray diffraction pattern of the high-temperature (1650°) synthesis product is given in Fig. 4b and in Table 4.

TABLE 4. Phase Composition of a $2Ce_2O_3 + 3SiO_2$ Mixture after Roasting in Hydrogen at 1650° and a Residence Time of 8 hr

I	d, A	Phases present						I	d, A	Phases present					
		$2Ce_2O_3 \cdot 3SiO_2$		$Ce_2O_3 \cdot 2SiO_2$		SiO_2				$2Ce_2O_3 \cdot 3SiO_2$		$Ce_2O_3 \cdot 2SiO_2$		SiO_2	
		I	d, A	I	d, A	I	d, A			I	d, A	I	d, A	I	d, A
10	4,33	—	—	8	4,35		—	20	2,18		—	21	2,18		—
20	4,20	20	4,20		—		—	20	2,13	30	2,13		—		—
10	4,01		—		—	100	4,04	30	2,04		—	65	2,035		—
10	3,60	10	3,56		—		—	40	2,01	40	2,00		—		—
50	3,40		—	100	3,40		—	30	1,95	20	1,95		—		—
50	3,28	40	3,28	38	3,28		—	50	1,905	50	1,90		—		—
30	3,17	40	3,17	17	3,17		—	30	1,86	20	1,86		—		—
10	3,10		—	25	3,08		—	50	1,833	40	1,83	48	1,834		—
100	2,90	100	2,89		—		—	50	1,810	40	1,81		—		—
20	2,79	30	2,80		—		—	20	1,787	10	1,78		—		—
10	2,68		—	40	2,70		—	20	1,72		—	18	1,725		—
10	2,51		—		—	18	2,49	30	1,67		—	15	1,69		—
20	2,30	20	2,30		—		—								

TABLE 5. X-Ray Diffraction Pattern of $2Ce_2O_3 \cdot 3SiO_2$

I	d, A	I	d, A	I	d, A
20	4,20	50	1,90	20	1,32
10	3,56	20	1,86	20	1,30
40	3,28	40	1,83	30	1,277
40	3,17	40	1,81	30	1,259
100	2,89	10	1,78	10	1,212
30	2,80	20	1,57	10	1,197
20	2,30	20	1,55	10	1,185
10	2,20	20	1,52	10	1,166
30	2,13	20	1,50	10	1,148
10	2,04	20	1,47		
40	2,00	10	1,36		
20	1,95	10	1,33		

TABLE 6. Refractive Indices of the Crystalline Phases

Compound	n_{ep}	Birefringence
$Ce_2O_3 \cdot SiO_2$	1,880	0,025
$2Ce_2O_3 \cdot 3SiO_2$	1,850	0,020
$Ce_2O_3 \cdot 2SiO_2$	1,770	0,015

Evidently for the same reason, the "first" phase, recorded by thermogravimetric analysis, does not appear on the x-ray diffraction pattern of a sample roasted at 1650°.

The x-ray diffraction pattern of $2Ce_2O_3 \cdot 3SiO_2$ reveals a hexagonal system (Table 5); the lattice parameters were determined: α 11.36 A; c 4.71 A; c-a 0.415.

Three phases were detected in the product by microscopic analysis. Table 6 gives the mean values of the refractive indices of the crystalline phases in a $2Ce_2O_3 \cdot 3SiO_2$ mixture after heating in hydrogen at 1650° and a residence time of 8 hr.

Investigation of a $1Ce_2O_3 + 1SiO_2$ Mixture

Gravimetric oxidizing analysis showed that at low synthesis temperatures (1250-1270°) only phases which decompose when heated in air in the room temperature to 500° range are formed in a $1Ce_2O_3 + 1SiO_2$ mixture; this may be seen from Fig. 5a. With high synthesis temperatures (1600-1670°), the product contains two phases (Fig. 5b), which indicates the presence of two silicates in the mixture: $Ce_2O_3 \cdot SiO_2$ and $2Ce_2O_3 \cdot 3SiO_2$ and the absence of the compound $Ce_2O_3 \cdot 2SiO_2$ (third phase).

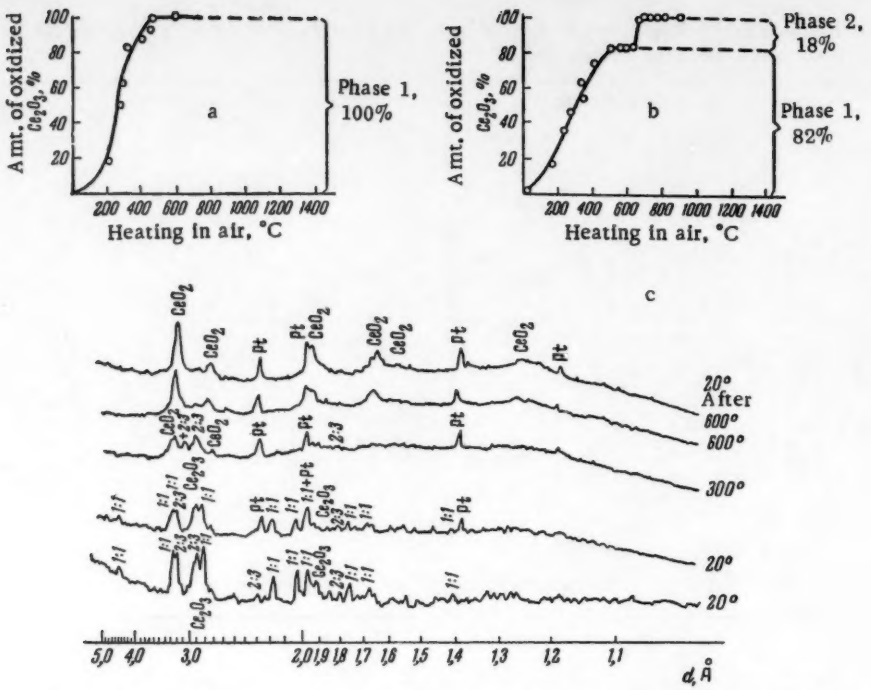

Fig. 5. Gravimetric (a,b) and x-ray (c) analyses of the products in a $1Ce_2O_3 + 1SiO_2$ mixture after heating in hydrogen.

TABLE 7. Phase Composition of a $Ce_2O_3 + SiO_2$ Mixture after Roasting in Hydrogen at 1250° and a Residence Time of 16 hr

I	d, A	Phases present									
		$Ce_2O_3 \cdot SiO_2$		$2Ce_2O_3 \cdot 3SiO_2$		Ce_2O_3		CeO_2		SiO_2	
		I	d, A	I	d, A	I	d, A	I	d, A	I	d, A
30	4,40	80	4,36		—		—		—		—
5	4,00		—		—		—		—	100	4,04
10	3,30		—	40	3,28		—		—		—
80	3,24	100	3,20		—		—	100	3,12		—
70	3,17		—	40	3,17		—		—		—
10	3,03		—		—	30	3,29		—		—
60	2,94		—		—	100	2,94		—		—
80	2,90		—	100	2,89		—		—		—
100	2,82	100	2,80	30	2,80		—		—		—
20	2,75		—		—		—	29	2,71		—
20	2,30		—	20	2,30		—		—		—
10	2,23		—		—	30	2,25		—		—
50	2,18	100	2,17		—		—		—		—
60	2,03	70	2,02	10	2,04		—		—		—
20	2,01		—	40	2,00		—		—		—
10	1,97	70	1,96		—		—		—		—
30	1,93		—		—	50	1,94	50	1,91		—
20	1,90		—	50	1,90		—		—		—
20	1,860		—	20	1,86		—		—		—
20	1,810		—	40	1,81		—		—		—
40	1,76	70	1,757		—		—		—		—

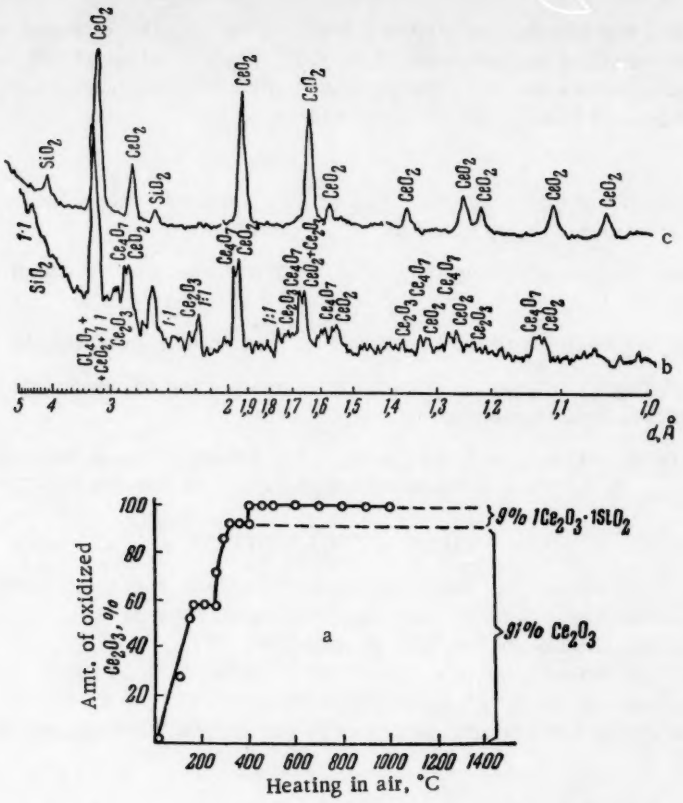

Fig. 6. Gravimetric (a) and x-ray (b,c) analyses of the products in a $2Ce_2O_3 + 1SiO_2$ mixture after heating in hydrogen.

With low synthesis temperatures (1250-1270°), the following phases are recorded in samples of this composition by x-ray structural analysis: $Ce_2O_3 \cdot SiO_2$, $2Ce_2O_3 \cdot 3SiO_2$, and considerable amounts of Ce_2O_3, CeO_2, and SiO_2. Cerium dioxide was formed as a result of oxidation of free Ce_2O_3 by atmospheric oxygen. The characteristic x-ray diffraction pattern for these compositions is given in Fig. 5c (see lower curve). This figure also shows the variation of the phase composition during heating of the sample in air. As may be seen from Fig. 5c, complete decomposition of the products, with formation of CeO_2 and SiO_2, takes place at 600°. Table 7 gives data on the x-ray analysis of the sample.

TABLE 8. X-Ray Diffraction Pattern of $Ce_2O_3 \cdot SiO_2$

I	*d*, Å	*I*	*d*, Å
80	4,36	100	2,17
100	3,20	70	2,02
100	2,80	70	1,96
40	2,33	70	1,757
		40	1,676

At higher synthesis temperatures the amount of initial substances in the product is reduced, and the x-ray diffraction patterns of the 1:1 and 2:3 phases become more distinct. The 1:1 phase is revealed most distinctly in the x-ray diffraction pattern of a $1Ce_2O_3 + 1SiO_2$ mixture, heated in hydrogen at 1670°; the lines of the 1:1 phase are given in Table 8 and are taken as the standard for the x-ray diffraction pattern of this phase.

Investigation of a $2Ce_2O_3 + 1SiO_2$ Mixture

The product obtained as a result of roasting a $2Ce_2O_3 + 1SiO_2$ mixture in hydrogen at 1550° decomposes in the room temperature to 400° range when oxidized in air; this is shown in Fig. 6a. The sample contains 91% of free Ce_2O_3; the product is unstable in air and begins to oxidize at room temperature when the sample is ground in a mortar. As the Ce_2O_3 is oxidized, the more stable oxide Ce_4O_7 is formed; this is oxidized in the 260-320° range. Nine percent of Ce_2O_3 is combined in the form of $Ce_2O_3 \cdot SiO_2$, which decomposes at approximately 400°.

Figure 6 gives the x-ray diffraction patterns of a sample in various stages of oxidation. The x-ray diffraction pattern (Fig. 6b) shows maxima for the compounds Ce_4O_7, CeO_2, Ce_2O_3, and $Ce_2O_3 \cdot SiO_2$, while the x-ray diffraction pattern of the sample completely oxidized by heating in air at 400° shows maxima for CeO_2 and SiO_2 (Fig. 6c). A compound with the composition $2Ce_2O_3 \cdot 1SiO_2$ was not detected.

SUMMARY

1. The reaction in solid phases in the system $Ce_2O_3 - SiO_2$ was investigated. The mixtures were heated in hydrogen, in which CeO_2 was reduced to Ce_2O_3, and the latter reacted with silica.

2. Three chemical compounds: $Ce_2O_3 \cdot SiO_2$, $2Ce_2O_3 \cdot 3SiO_2$, and $Ce_2O_3 \cdot 2SiO_2$ are formed in the system $Ce_2O_3 - SiO_2$.

3. Crystalline $Ce_2O_3 \cdot 2SiO_2$ was synthesized from a stoichiometric mixture with the composition $1Ce_2O_3 + 2SiO_2$.

4. The compounds $Ce_2O_3 \cdot SiO_2$ and $2Ce_2O_3 \cdot 3SiO_2$ are unstable and are not formed as pure crystalline phases in stoichiometric mixtures of these compounds.

5. Cerium silicates decompose when heated in air. Their stability increases in the order: $Ce_2O_3 \cdot SiO_2 < 2Ce_2O_3 \cdot 3SiO_2 < Ce_2O_3 \cdot 2SiO_2$. Their decomposition temperatures are 300-500, 600-700, and 900°, respectively.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

PHYSICOCHEMICAL INVESTIGATION OF THE REACTION BETWEEN LANTHANUM HYDROXIDE AND HYDROGEN PEROXIDE

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There are very few reports on the synthesis and investigation of the properties of rare-earth peroxides. Thus, lanthanum peroxide was first obtained by Cléve [1] in 1885 by treating solutions of lanthanum salts with ammonia and hydrogen peroxide. After the gelatinous precipitates had been washed and dried, they were found to be of the peroxide type and corresponded to a composition approximating to the formula La_2O_5. Melikov and Pisarzhevskii prepared lanthanum peroxide in a similar manner [2] and considered it to be $La_2O_5 \cdot nH_2O$ or $HLaO_3 \cdot nH_2O$, assuming that it was a true metal peroxide. When dilute H_2SO_4 acts on lanthanum peroxide, hydrogen peroxide is liberated, whereas when concentrated H_2SO_4 is used, ozonized oxygen is formed. The authors observed the decomposition of lanthanum peroxide during drying (completed at 200°C), with loss of "active" oxygen and water.

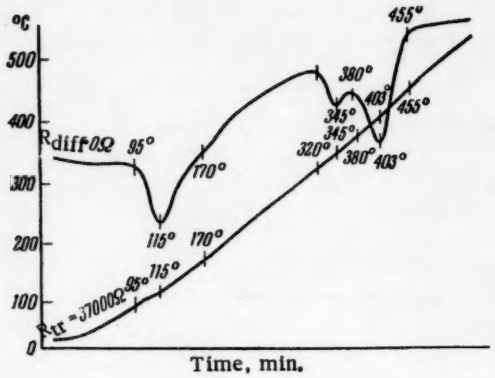


Fig. 1. Differential heating curves of lanthanum hydroxide.

EXPERIMENTAL

To determine the different forms of peroxide compounds of elements of the lanthanum subgroup and the conditions of their formation, a series of investigations was carried out on the reaction of hydroxides of these elements with hydrogen peroxide within a wide range of hydrogen-peroxide concentration (from 0 to about 97%) and temperatures from 0° to −20°. The investigation was carried out by the usual solubility method, the experimental results being represented graphically in the diagrams: $Me_2O_3 - H_2O - \frac{1}{2}O_2$ and $Me_2O_3 - H_2O_2$. The "residue" method makes it possible to determine fairly reliably the true composition of the solid phases formed and the concentration limits of their existence.

TABLE 1. Time Required to Obtain Equilibrium during the Reaction of Lanthanum Hydroxide with Hydrogen Peroxide at −20°

Time, hrs	Comp. of liquid phase, wt.%			Comp. of residue, wt.%		Solid phase
	Active O_2	H_2O_2	La_2O_3	Active O_2	La_2O_3	
1	18,81	39,99	0,110	10,63	46,55	$La(OH)_3 + La_2O_4 \cdot H_2O$
2	18,65	39,65	0,160	11,01	46,35	$La_2O_4 \cdot H_2O$
3	18,73	39,82	0,099	11,55	43,20	The same
5	18,56	39,46	0,137	11,13	45,74	

The procedure employed was as follows: freshly precipitated hydroxides were mixed for a specific period under isothermal conditions with aqueous solutions of hydrogen peroxide until chemical analysis of the liquid and solid phases (determined graphically for the residue) was constant. The residue and the liquid phase were then analyzed

* Deceased.

TABLE 2. Data of the Reaction of $La(OH)_3$ with H_2O_2 Solutions at 0°

Expt. No.	Comp. of liquid phase, wt. %			Comp. of residue, wt. %		Solid phase
	Active O_2	H_2O_2	La_2O_3	Active O_2	La_2O_3	
54	0,00	0,00	0,082	0,00	0,00	$La(OH)_3$
52	0,34	0,72	0,089	2,79	50,06	$La(OH)_3 + La_2O_4 \cdot 2H_2O$
53	4,60	9,78	0,102	5,01	45,61	$La_2O_4 \cdot 2H_2O$
55	6,37	13,54	0,089	5,65	50,61	the same
40	7,68	16,33	0,094	—	—	» »
26	8,98	19,09	—	6,50	48,86	» »
38	9,70	20,62	0,075	—	—	» »
49	9,91	21,00	0,107	—	—	» »
27	12,88	27,38	0,050	8,40	45,73	—
23	14,99	31,87	—	9,41	48,50	» »
37	16,49	35,05	0,080	—	—	» »
44	19,88	42,26	0,051	—	—	» »
50	19,90	42,30	0,023	—	—	» »
61	21,60	45,90	0,069	13,03	46,43	» »
65	22,30	47,40	0,065	—	—	» »
47	22,57	47,98	0,037	—	—	» »
33	23,74	50,47	0,049	14,50	44,68	» »
3	23,89	50,79	—	13,38	47,67	» »
67	24,69	52,90	—	13,92	47,71	» »
31	26,68	55,68	0,067	16,79	38,41	» »
56	30,81	65,50	0,065	17,17	45,80	» »
64	31,14	66,20	0,075	18,40	41,38	» »
59	32,09	68,22	0,059	18,08	45,35	the same
60	33,05	70,26	0,073	18,53	44,93	» »
58	34,30	72,90	0,081	18,98	45,03	» »
41	34,49	73,30	0,018	—	—	» »
57	35,02	74,41	0,055	20,39	42,44	» »
8	38,66	82,19	—	21,69	43,07	» »
66	39,28	83,50	0,021	—	—	decomp.
70	40,95	87,05	0,033	—	—	»
39	41,45	88,15	0,014	22,93	42,88	»
11	43,16	91,70	—	24,12	42,23	»
69	44,13	93,80	0,035	—	—	
9	45,22	96,20	—	26,72	39,58	»

TABLE 3. Data of the Reaction of $La(OH)_3$ with H_2O_2 Solutions at −20°

Expt. No.	Liquid phase comp., wt. %			Residue comp., wt. %		Solid phase
	Active O_2	H_2O_2	La_2O_3	Active O_2	La_2O_3	
2	14,82	31,52	0,055	7,85	61,33	$La_2O_4 \cdot H_2O$
11	20,14	42,82	—	11,91	48,63	the same
5	22,61	48,07	0,078	13,50	47,91	» »
13	25,83	54,91	0,126	14,70	47,03	» »
8	28,39	60,36	0,133	17,49	41,47	» »
6	31,72	67,43	0,132	17,06	48,59	» »
7	35,20	74,84	0,105	22,50	39,27	» »
10	38,34	81,51	0,032	22,01	44,51	» »
9	44,61	94,84	0,038	21,88	44,81	decomposed

for their content of Me_2O_3, $\frac{1}{2}O_2$, followed by plotting of the data on a Gibbs' triangle, where the composition of the solid phase to be determined was found from the point of intersection of the straight lines.

Lanthanum hydroxide $La(OH)_3$ was prepared from solutions of lanthanum nitrate and excess ammonia. The lanthanum hydroxide formed as a result of precipitation from hot solutions had the appearance of a white gelatinous mass. After the product had been filtered and washed, it was dried under vacuum at 35-40°; the heater was then switched off and the substance was ground to a fine cream-colored powder. Endothermic effects at 95-115°, 320 to 345°, and 380-403°, corresponding to gradual dehydration and formation of lanthanum monohydroxide LaO · OH, are observed on the differential heating curves of lanthanum hydroxide (Fig. 1).

Pure hydrogen peroxide, without a stabilizer, was prepared by distillation of perhydrol in a vacuum apparatus. The active oxygen in the investigation products was determined by titration with a 0.1 N solution of $KMnO_4$ in sulfuric acid. The lanthanum in the residue and in the liquid phase was determined gravimetrically: by precipitation as the oxalate, followed by calcination to La_2O_3 in a muffle at 800-900°.

Reaction of lanthanum hydroxide with hydrogen peroxide at 0° and −20°. The time required to obtain equilibrium during the reaction of lanthanum hydroxide with hydrogen peroxide was determined by: a) constancy of the composition of the liquid phase; and b) constancy of the composition of the solid phase formed. The time required to obtain equilibrium between the chemical compositions of the liquid and solid phases was determined as 2-3 hr, and is illustrated by the data of Table 1 for −20°.

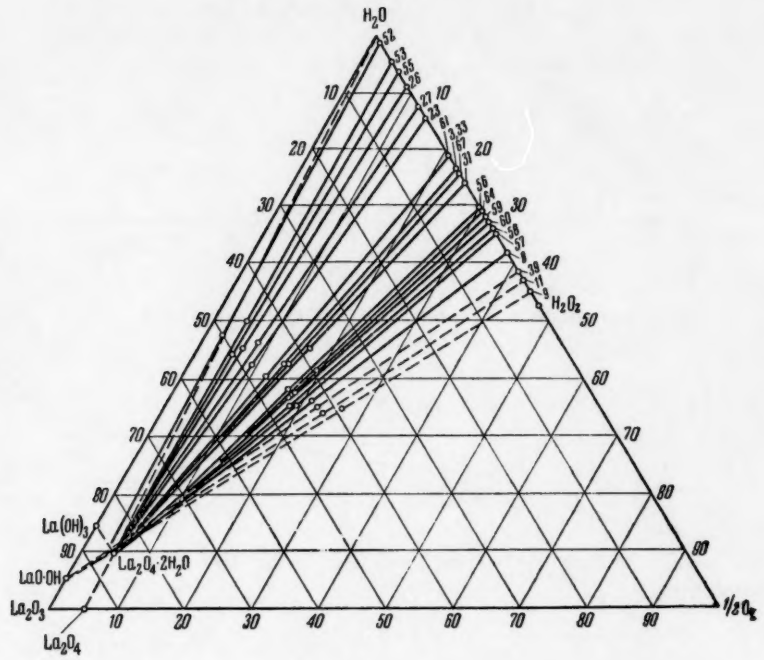


Fig. 2. 0° Isotherm of the system $La(OH)_3 - H_2O_2 - H_2O$.

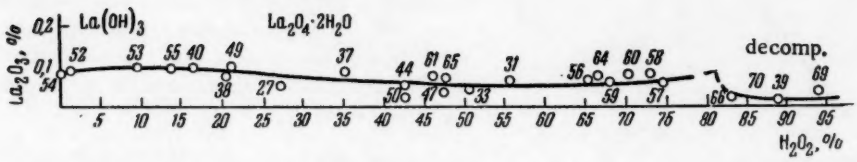


Fig. 3. 0° Isotherm of the system $La(OH)_3 - H_2O_2 - H_2O$ in rectangular coordinates.

The reaction between $La(OH)_3$ and H_2O_2 solutions at 0° was investigated in the hydrogen-peroxide concentration range from 0.00 to 96.20% in the liquid phase, and was examined with respect to the formation of solid phase in the ternary system $La(OH)_3 - H_2O_2 - H_2O$. The results of the investigation are given in Table 2 and in Figs. 2 and 3. From 0.00 to 0.72% H_2O_2, lanthanum hydroxide exists in the liquid phase. In the region from 0.73 to about 83% H_2O_2, one peroxide-type phase with the general composition $La_2O_3 \cdot 2H_2O$ is formed. From about 83.5 to 96.20% H_2O_2, appreciable decomposition of the residues is observed. Thus, three branches corresponding to $La(OH)_3$, $La_2O_4 \cdot 2H_2O$, and the decomposition states of the "residues" are found on the solubility curve (Fig. 3).

Apart from the region of ice (from 0.00 to 31.52% H_2O_2 in the liquid phase), at −20° one phase of the peroxide type, with the general composition $La_2O_4 \cdot H_2O$, was again detected (from 31.52 to 81.51% H_2O_2 in the liquid phase (Table 3, Figs. 4 and 5). Above 81.51% H_2O_2, decomposition of the residues is noted (Table 3).

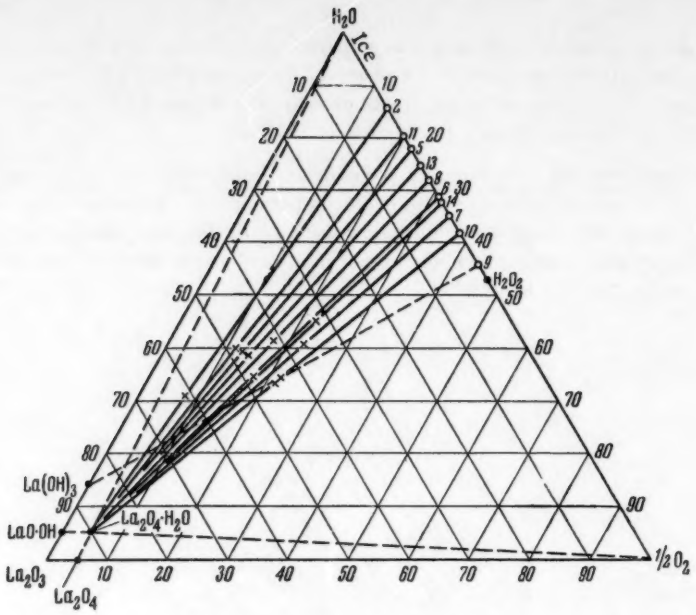


Fig. 4. −20° Isotherm of the system $La(OH)_3 - H_2O_2 - H_2O$.

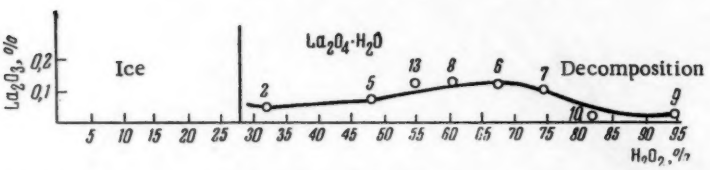


Fig. 5. −20° Isotherm of the system $La(OH)_3 - H_2O_2 - H_2O$ in rectangular coordinates.

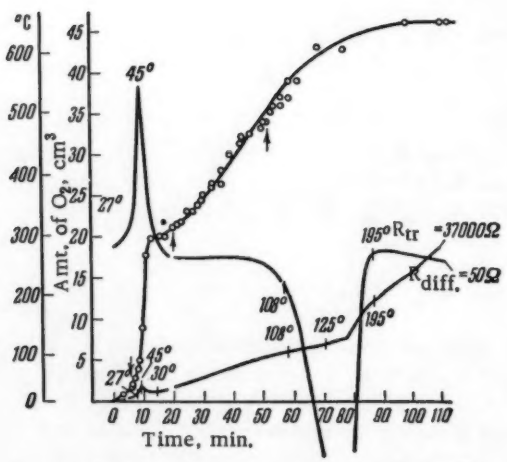


Fig. 6. Differential heating curves of the residue corresponding to $La_2O_4 \cdot H_2O$.

Two branches, corresponding to $La_2O_4 \cdot H_2O$ and the decomposed residues, are observed on the solubility curve (Fig. 5). The residue corresponding to $La_2O_4 \cdot 2H_2O$ was washed with alcohol, ether, and subjected to various types of drying (Table 4). The data of Table 4 for the residue $La_2O_4 \cdot 2H_2O$ show that washing with alcohol, ether, and various types of drying lead to the formation of a product with a higher active oxygen content. The product obtained was similar in composition to $La_2O_5 \cdot nH_2O$ (where n = 3-6).

The increase in the content of active oxygen and water may be explained by the action of hydrogen peroxide during decomposition.

Differential heating curves of the "residues" of $La_2O_4 \cdot 2H_2O$ and $La_2O_4 \cdot H_2O$ (Table 5) were determined in a Kurnakov recording pyrometer with a Rt-RtRh thermocouple at a heating rate of 3-4 deg/min, with simultaneous recording of the volume of the liberated oxygen.

Outwardly, the differential heating curves of the $La_2O_4 \cdot H_2O$ "residues" are the same and are characterized by the

TABLE 4. Data on Dehydration of $La_2O_4 \cdot 2H_2O$ "Residue"

$La_2O_4 \cdot 2H_2O$ Residue	Prod. comp., wt.%			Product comp., M			Formula
	act. O_2	La_2O_3	H_2O	act. O_2	La_2O_3	H_2O	
Initial	13,92	47,41	38,67	5,96	1,00	24,71	—
Washed with ether	5,24	71,15	23.61	1,50	1,00	5,95	$La_2O_{4.5} \cdot 6H_2O$
Washed with alcohol, ether	5,81	71,42	22,87	1,66	1,00	6,53	$La_2O_{4.7} \cdot 6{,}5\ H_2O$
Washed with alcohol, ether; dried under vacuum at 20°	5,34	76,10	13,87	1,43	1,00	3,29	$La_2O_{4.4} \cdot 3{,}3H_2O$
Washed with alcohol, ether; dried under vacuum at 30°	4,92	74,43	20,65	2,35	1,00	5,03	$La_2O_{4.4} \cdot 5H_2O$
Initial	16,03	45,06	38,91	7,25	1,00	15,66	
Dried over P_2O_5 at 4° for 7 days	6,15	78,82	15,03	1,59	1,00	3,45	$La_2O_{4.6} \cdot 3{,}5H_2O$

TABLE 5. Chemical Composition of the Liquid Phases and Residues Corresponding to the Solid Phases $La_2O_4 \cdot 2H_2O$ and $La_2O_4 \cdot H_2O$

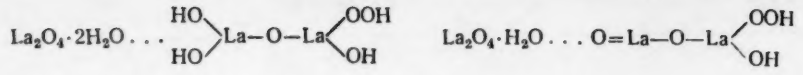
Solid phase	Residue comp., wt. %			Liquid phase comp., wt.%	
	act. O_2	La_2O_3	H_2O	act. O_2	H_2O
$La_2O_4 \cdot 2H_2O$	10,08	47.80	42,12	15,18	84,22
$La_2O_4 \cdot H_2O$	14,70	47,03	38,27	25,83	74,17

TABLE 6. Change in Chemical Composition of $La_2 \cdot 2H_2O$ and $La_2O_4 \cdot H_2O$ "Residue" on Heating

Residue corresponding to solid phase	Temp. °C	Prod. comp., wt.%			Product comp., M			Formula
		act. O_2	La_2O_3	H_2O	act. O_2	La_2O_3	H_2O	
	0	18,40	41,38	40,22	9,06	1,00	17,85	—
$La_2O_4 \cdot 2H_2O$	50	3,66	57,69	39,65	1,29	1,00	12,44	$La_2O_{4.3} \cdot 12.4HO$
	85	3,20	66,88	29,69	0,98	1,00	8,05	$La_2O_4 \cdot 8H_2O$
	~200	0,07	82,12	17,83	0,02	1,00	3,94	$La_2O_3 \cdot 4H_2O$
$La_2O_4 \cdot H_2O$	—20	14,70	47,03	38,27	6,38	1,00	14,75	—
	85	3,76	51,02	45,22	1,49	1,00	16,00	$La_2O_{4.5} \cdot 16H_2O$
	218	0,22	81,03	18,75	0,05	1,00	4,18	$La_2O_3 \cdot 4{,}2H_2O$

presence of an exothermic effect at 27-45° and 25-70°, and an endothermic effect at 105-125° and 98-110° (Figs. 6 and 7). The liberation of active oxygen (dotted line) coincides with the commencement of an exothermic effect and continues to about 200°. A chemical analysis to interpret the thermal effects for both "residues" showed that oxygen is liberated in two stages (Table 6); during this process, active oxygen is first liberated from the mother hydrogen peroxide at the temperature of the first exothermic effect. The product freed from excess hydrogen peroxide is subsequently dehydrated and decomposes at 85°, with liberation of oxygen, water, and the formation of hydrated lanthanum oxide $La_2O_3 \cdot (3\text{-}4)\,H_2O$.

The behavior of the residues corresponding to the solid phases $La_2O_4 \cdot 2H_2O$ and $La_2O_4 \cdot H_2O$, obtained in the investigation, during dehydration and the determination of the differential heating curve provide some foundation for the assertion that these compounds should hardly be considered as hydrates of lanthanum peroxides. They are more probably included in the category of hydroperoxide compounds of the type



SUMMARY

1. When $La(OH)_3$ reacts with H_2O_2 at 0 and −20° within wide limits of hydrogen-peroxide concentration, peroxide-type phases with the general composition $La_2O_4 \cdot 2H_2O$ and $La_2O_4 \cdot H_2O$ are formed.

2. Experiments on the dehydration of the peroxide-type "residues" obtained showed that anhydrous peroxide compounds of lanthanum cannot be obtained under these conditions.

3. Thermal investigations of these "residues" showed that thermal decomposition with liberation of active oxygen takes place in two stages: associated with decomposition of the adsorbed hydrogen peroxide and with the subsequent decomposition of the lanthanum hydroperoxide compounds.

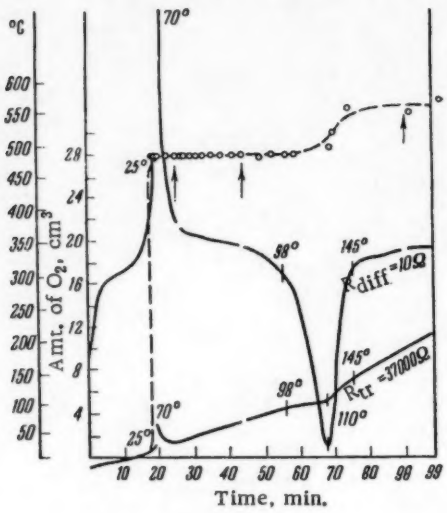


Fig. 7. Differential heating curves of the residue corresponding to $La_2O_4 \cdot H_2O$.

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PHYSICOCHEMICAL INVESTIGATION OF THE REACTION BETWEEN NEODYMIUM HYDROXIDE AND HYDROGEN PEROXIDE

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Neodymium peroxide was first synthesized by Cléve [1] from solutions of neodymium salts, ammonia, and hydrogen peroxide. The neodymium peroxide compound obtained by him approximates in composition to Nd_2O_5. Later, Brauner [2-4] indicated the possibility of the formation by neodymium of Nd_2O_4 and Nd_2O_5 in the hydrated form.

EXPERIMENTAL

Preparation of the Initial Substances and the Analysis Methods

A lilac-colored amorphous precipitate of neodymium hydroxide $Nd(OH)_3$ was precipitated from a hot solution of neodymium nitrate by excess ammonia. After the precipitate had been separated and washed on a filter, it was dried under vacuum at room temperature. The lumps of dry hydroxide formed were ground to a fine powder and the hydroxide was used for the investigation in this form. The differential heating curves of this neodymium hydroxide (Fig. 1) are characterized by two endothermic effects at 90 and 305°, corresponding to dehydration and, probably, to the formation of neodymium monohydroxide NdO · OH.

TABLE 1. Time Required to Obtain Equilibrium during the Reaction of $Nd(OH)_3$ with H_2O_2 at 0°

Time, hours	Amt. of active O_2 in residue wt.%	Comp. of liquid phase, wt.%	
		act. O_2	Nd_2O_3
Initial	—	10,33	—
1,0	4,30	6,79	0,154
1,5	6,29	6,46	0,149
3,0	6,07	—	0,172
4,0	6,08	6,46	0,132

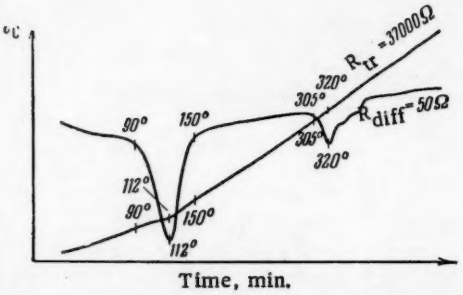

Fig. 1. Heating curve of neodymium hydroxide.

Pure hydrogen peroxide, without a stabilizer, was prepared by distillation of perhydrol in a vacuum apparatus. The active oxygen in the investigation products was determined by titration with a 0.1 N solution of $KMnO_4$ in sulfuric acid. The neodymium (converted to Nd_2O_3) in the residue and in the liquid phase was determined gravimetrically: by precipitation with oxalic acid, followed by calcination of neodymium oxalate to Nd_2O_3 in a muffle at 800-900°.

Reaction of neodymium hydroxide with hydrogen peroxide at 0 and −20°. The investigation of $Nd(OH)_3$ with hydrogen peroxide solutions was carried out by the usual solubility method, the experimental results being represented graphically in the diagrams: $Nd_2O_3 - \frac{1}{2}O_2 - H_2O$ and Nd_2O_3 and H_2O_2 by a method previously described [5]. The time required for equilibrium to be obtained between the chemical compositions of the liquid and solid phases was determined as 1.5-2 hr (Table 1).

The investigation of the reaction of $Nd(OH)_3$ with hydrogen peroxide solutions, carried out at 0 and −20°, is illustrated by the data of Tables 2 and 3 and Figs. 2-5.

In the triangular diagrams, $Nd_2O_3 - \frac{1}{2}O_2 - H_2O$, the solid phases formed at 0 and −20° were determined graphically by method of residues (Figs. 2,4), while in the system of rectangular

*Deceased.

TABLE 2. Data of the Reaction of $Nd(OH)_3$ with H_2O_2 Solutions at 0°

Expt. No.	Comp. of liquid phase, wt.%			Comp. of residue, wt.%		Solid phase
	act. O_2	H_2O_2	Nd_2O_3	act. O_2	Nd_2O_3	
76	—	—	0,004	—	—	$Nd(OH)_3$
37	0,72	1,53	0,220	3,22	27,84	$Nd_2O_5 \cdot 2H_2O$
65	1,70	2,54	—	4,19	33,97	the same
13	2,63	5,60	—	5,03	46,64	»
53	3,60	7,65	0,230	5,05	31,01	»
34	4,59	9,75	—	5,55	24,22	»
71	5,86	12,46	—	6,45	31,39	»
25	7,67	16,30	—	7,50	28,46	»
41	7,89	16,77	0,216	7,62	23,71	»
43	8,20	17,43	0,210	7,40	38,00	»
42	9,61	20,43	0,216	8,29	26,96	»
47	12,53	27,60	0,169	9,70	42,69	»
49	16,74	35,59	0,126	11,17	51,49	»
26	17,03	36,20	—	11,17	43,15	decomposed
48	18,08	38,44	0,133	11,57	49,63	the same
55	19,90	42,31	0,147	2,43	44,06	»
17	31,18	66,28	—	9,22	57,73	»
7	38,67	82,21	—	3,55	65,77	»
6	45,70	97,16	—	6,30	56,45	»

TABLE 3. Data of the Reaction of $Nd(OH)_3$ with H_2O_2 Solutions at −20°

Expt. No.	Comp. of liquid phase, wt.%			Comp. of residue, wt.%		Solid phase
	act. O_2	H_2O_2	Nd_2O_3	act. O_2	Nd_2O_3	
1	11,65	24,88	0,070	6,79	59,20	$Nd_2O_4 \cdot 2H_2O$
8	11,95	25,40	0,123	8,01	41,58	the same
11	13,40	28,49	0,103	8,81	45,39	»
7	13,93	29,62	0,102	7,49	49,75	»
13	14,88	31,63	0,150	8,40	48,20	»
5	15,04	31,97	0,110	10,80	37,22	»
3	16,21	34,46	0,110	8,82	54,37	»
10	17,04	36,22	0,102	9,73	46,36	»
12	17,60	37,42	0,109	10,00	44,75	»
2	18,32	39,37	0,081	5,87	61,63	decomposed
4	23,23	49,37	—	7,95	61,10	the same
6	29,89	63,54	0,110	13,62	47,61	»

TABLE 4. Data on the Dehydration of the "Residues" $Nd_2O_4 \cdot 2H_2O$ and $Nd_2O_5 \cdot 2H_2O$

Residue corr. to the solid phase	Type of treatment of residue	Comp. of product, wt.%			Comp. of the product, M			Formula
		act. O_2	Nd_2O_3	H_2O	act. O_2	Nd_2O_3	H_2	
	Initial	10,00	44,75	45,25	1,22	1,00	18,89	$Nd_2O_{4,2} \cdot 18,9H_2O$
	1. Drying over P_2O_5 at 4° for 2 days	5,22	72,13	22,65	1,50	1,00	5,79	$Nd_2O_{4,5} \cdot 5,8\,H_2O$
$Nd_2O_4 \cdot 2H_2O$	Initial	9,35	53,55	37,10	3,67	1,00	12,90	—
	2. After washing with alcohol and ether	5,82	72,72	21,46	1,73	1,00	5,52	$Nd_2O_{4,7} \cdot 5,5\,H_2O$
$Nd_2O_5 \cdot 2H_2O$	Initial	5,18	46,07	48,75	2,36	1,00	19,76	$Nd_2O_{5,4} \cdot 19,8H_2O$
	After washing with alcohol and ether	5,30	59,53	35,17	1,86	1,00	11,05	$Nd_2O_{4,9} \cdot 11H_2O$

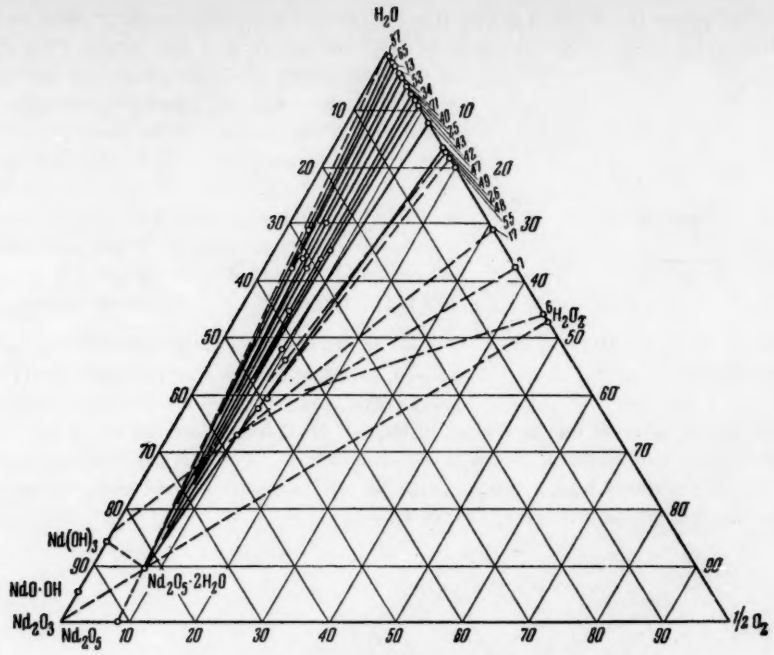

Fig. 2. 0° Isotherm of the system $Nd(OH)_3 - H_2O_2 - H_2O$.

TABLE 5. Chemical Composition of the Liquid Phases and Residues Corresponding to the Solid Phases $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O \cdot 2H_2O$

Solid phase	Composition of the residue, wt.%			Composition of the liquid phase, wt.%	
	act. O_2	Nd_2O_3	H_2O	act. O_2	H_2O
$Nd_2O_5 \cdot 2H_2O$	6,45	31,39	62,16	5,86	34,14
$Nd_2O_4 \cdot 2H_2O$	8,81	45,39	45,80	13,40	86,60

TABLE 6. Variation of the Chemical Composition of the "Residues" $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O_4 \cdot 2H_2O$ during Heating

Residue corresponding to solid phase	Temp., °C	Comp. of product, wt.%			Comp. of product, M			Formula
		act. O_2	Nd_2O_3	H_2O	act. O_2	Nd_2O_3	H_2O	
	0	4,20	39,97	55,83	2,41	1,00	28,44	
	60—75	3,50	41,33	55,17	1,94	1,00	27,12	$Nd_2O_5 \cdot 27H_2O$
$Nd_2O_5 \cdot 2H_2O$	175—200	0,13	78,70	21,17	0,00	1,00	5,46	$Nd_2O_3 \cdot 5,5H_2O$
	225—240	0,00	83,04	16,96	0,00	1,00	4,15	$Nd_2O_3 \cdot 4H_2O$
$Nd_2O_4 \cdot 2H_2O$	—20	8,39	48,17	43,44	3,66	1,00	16,87	
	55—60	2,98	57,95	39,07	1,08	1,00	12,62	$Nd_2O_4 \cdot 12,6H_2O$
	200	0,12	89,20	10,68	0,00	1,00	2,23	$Nd_2O_3 \cdot 2,2H_2O$

coordinates $Nd_2O_3 - H_2O_2$ the solubility of Nd_2O_3 in the liquid phase at 0 and −20° was determined for various hydrogen peroxide concentrations (Figs. 3,5). As follows from an examination (Table 2 and Figs. 2, 3) at 0°, the presence of two solid phases was established: the initial $Nd(OH)_3$ and a peroxide phase with the general composition $Nd_2O_5 \cdot 2H_2O$, within H_2O_2 concentration limits from 1.53 to 35.59%. At an H_2O_2 content of more than 36% in the liquid phase, decomposition of the "residues" is observed. At −20°, in addition to the ice region (up to about 25% H_2O_2 in the liquid phase) a peroxide-type phase, $Nd_2O_4 \cdot 2H_2O$, was distinguished in the region of 24.88 to 37.42% H_2O_2 in the liquid phase. Above 39% H_2O_2, appreciable decomposition is observed.

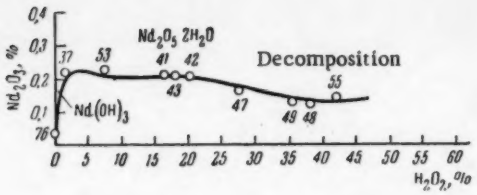

Fig. 3. 0° Isotherm of the system $Nd(OH)_3 - H_2O_2 - H_2O$ in rectangular coordinates.

The marked increase in the solubility of Nd_2O_3 in aqueous solutions of hydrogen peroxide should be particularly noted (Figs. 3,5). Thus, at 0°, the Nd_2O_3 content in aqueous solutions is not more than 0.004%, whereas for the regions of $Nd_2O_5 \cdot 2H_2O$ formation, the solubility of Nd_2O_3 increases approximately 50-fold. A similar phenomenon is observed at −20°. Residues corresponding to the solid phases $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O_4 \cdot 2H_2O$ separated from hydrogen peroxide solutions were washed with alcohol and ether, and were dried in a desiccator over phosphorus pentoxide (Table 4).

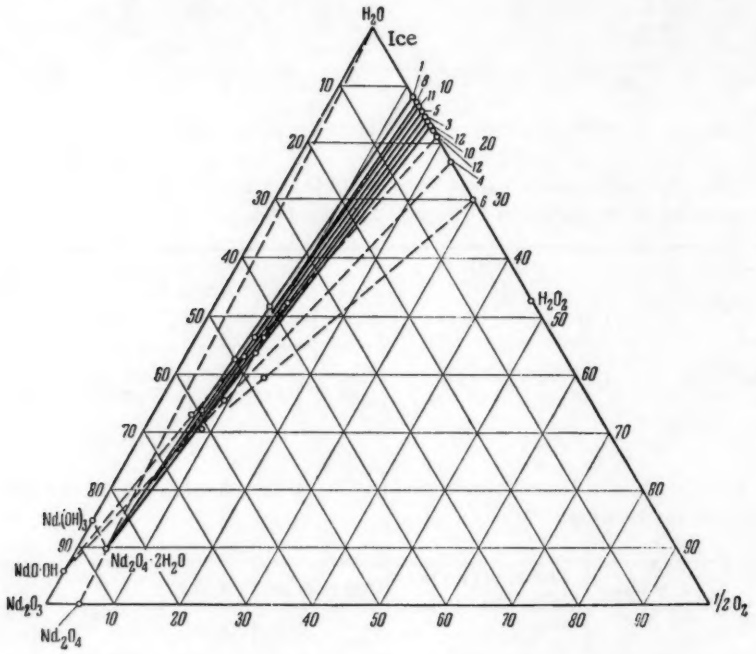

Fig. 4. −20° Isotherm of the system $Nd(OH)_3 - H_2O_2 - H_2O$.

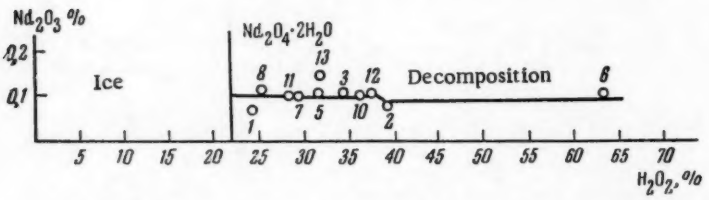

Fig. 5. −20° Isotherm of the system $Nd(OH)_3 - H_2O_2 - H_2O$ in rectangular coordinates.

From these preliminary data it follows that, during the dehydration process, products similar in composition to $Nd_2O_5 \cdot nH_2O$ are obtained. However, like lanthanum peroxide compounds, anhydrous neodymium peroxide compounds were not obtained in this case.

The differential heating curves of the "residues" $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O_4 \cdot 2H_2O$ (Table 5) were determined in a Kurnakov recording pyrometer with a Pt-PtRh thermocouple at a heating rate of 3-4 deg/min; the volume of liberated oxygen was recorded at the same time.

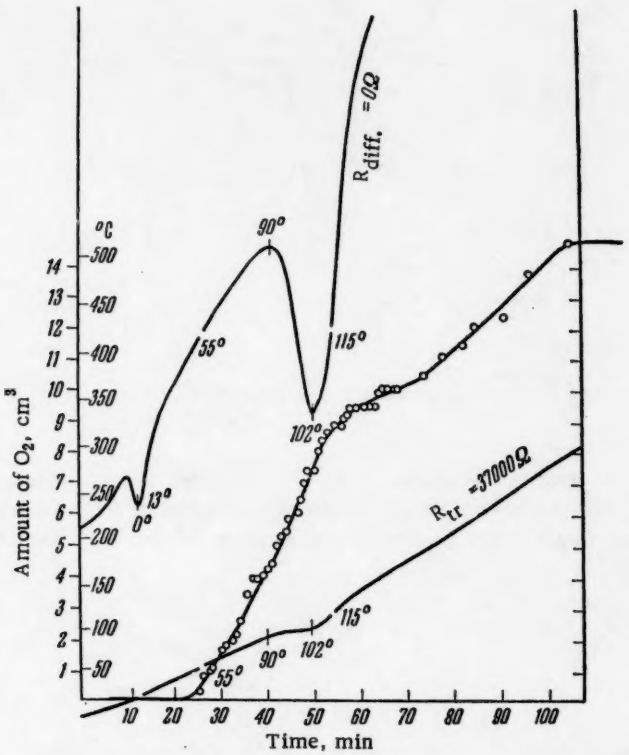

Fig. 6. Heating curve of the residue corresponding to $Nd_2O_5 \cdot 2H_2O$.

The differential heating curves of the residue corresponding to the solid phase $Nd_2O_5 \cdot 2H_2O$ (Fig. 6) are characterized by the presence of two endothermic effects at 0 and 90-102°. The first endothermic effect corresponds to fusion of the residue in the presence of excess liquid phase, while the second is related to dehydration and liberation of oxygen. It may be assumed that the exothermic effect corresponding to liberation of oxygen is masked by the endothermic effect of dehydration. An exothermic effect at 25-60°, and an endothermic effect at 93-105° may be seen on the heating curves of the "residue" $Nd_2O_4 \cdot 2H_2O$ (Fig. 7). Chemical analysis of the "residues" $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O_4 \cdot 2H_2O$ during the heating process showed that oxygen is liberated in two stages (Table 6).

These results indicate that during heating, oxygen is first liberated from the hydrogen peroxide absorbed by the residue. At 60-75° the "residue" $Nd_2O_4 \cdot 2H_2O$ had the general composition $Nd_2O_5 \cdot 27H_2O$, while that of the "residue" $Nd_2O_4 \cdot 2H_2O$ was $Nd_2O_4 \cdot 12.6H_2O$. With further heating (about 85-90°) the neodymium peroxide compounds decompose with liberation of water and active oxygen. At 200° the composition of the product was expressed by the formula: $Nd_2O_3 \cdot nH_2O$, approximating to $Nd(OH)_3$.

A comparison of data of the composition of the peroxide-type solid phases formed during the reaction of $Nd(OH)_3$ with hydrogen peroxide solutions shows that fairly clear data on the formation of two peroxide-type solid phases $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O_4 \cdot 2H_2O$ are obtained by the use of conventional investigation methods for the study of the solubility. Separation of these phases by ordinary preparative methods leads to considerable changes in the

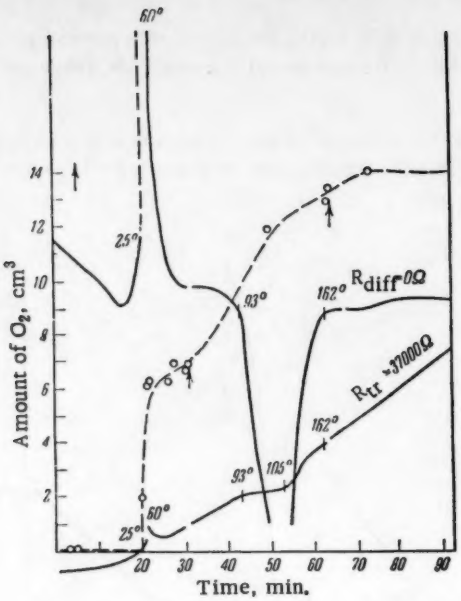

Fig. 7. Heating curve of the residue corresponding to $Nd_2O_4 \cdot 2H_2O$.

chemical composition, due to the resultant disturbance of the ratios between the solid phases and the composition of the liquid phases. Preliminary investigations of the solid phases distinguished do not justify their inclusion in the hydrates of neodymium peroxide Nd_2O_5 or Nd_2O_4. It is more probable to assume that with trivalent neodymium they must have a formula of the type

$Nd_2O_4 \cdot 2H_2O \ldots$ HO, HO, Nd—O—Nd, OOH, OH

$Nd_2O_5 \cdot 2H_2O \ldots$ HOO, HO, Nd—O—Nd, OH, OOH

SUMMARY

1. An investigation of the reaction of $Nd(OH)_3$ with H_2O_2 within wide concentration limits made it possible to distinguish two phases of the peroxide type: $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O_4 \cdot 2H_2O$.

2. Anhydrous neodymium peroxide compounds were not obtained when the "residues" $Nd_2O_5 \cdot 2H_2O$ and $Nd_2O_4 \cdot 2H_2O$ were separated and subsequently dehydrated.

3. The probable formulas of the peroxide-type solid phases which were distinguished are characterized by the presence of perhydroxyl and hydroxyl groups, and by oxygen bonds between neodymium atoms.

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ADSORPTION OF A MIXTURE OF GASES

COMMUNICATION 6. ADSORPTION EQUILIBRIUM IN THE SYSTEM WATER – N-HEPTANE – SILICA GEL

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After studying the adsorption of mixtures of water and ethyl chloride vapor on activated charcoals [1,2], it appeared desirable to us to study the adsorption of mixtures of water vapor with the vapor of a nonpolar substance, for example n-heptane on an adsorbent of a different chemical nature, with a hydrophilic surface since, in this case, one could expect the roles of the two components to be interchanged during adsorption. As an adsorbent of this sort we selected commercial coarsely porous KSK silica gel, carefully purified by treatment with nitric and hydrochloric acid vapor, and washed with distilled water to constant electrical conductivity. The specific surface of this silica gel, determined by the BET method, was equal to 380 m^2/g, and the total pore volume v_s was 0.90 cm^2/g [3].

For the experiments we used double-distilled water and a very pure preparation of n-heptane with the constants d^{20}_4 0.6838 g/cm^3, b.p. 98.4°, and $n^{20}D$ 1.3875. All the adsorption measurements were made at 75° by the volume-weight method [1]. Before each series of experiments, the silica gel was evacuated for four hours at a temperature of 200° and a pressure of about $1 \cdot 10^{-5}$ mm Hg. This method of evacuation does not produce loss of structural water, while the physically adsorbed water is completely removed and, therefore, the subsequent adsorption of water vapor is strictly reversible in the adsorption region.

Figure 1 gives the individual adsorption isotherms of n-heptane (curve A) and water (curve B); here and subsequently the index 1 refers to heptane and the index 2 refers to water. For both isotherms, in the range of relative pressures $\underline{h}$ from 0.1 to 0.4, the BET equation is formally satisfied with the constants a_m = 1.96 millimole/g and c = = 6.5 for the water isotherm, and a_m = 0.99 millimole/g and c = 1.3 for the n-heptane isotherm.

Figure 2 gives the experimental data on the combined adsorption of water and n-heptane in the form of curve $a_2 = f(a_1)$ for five series of experiments, in each of which the quantity of water in the system remained constant. The data obtained were represented in the form of curves giving h_2 as a function of h_1, a_1 as a function of h_1, a_2 as a function of h_1, a_2 as a function of h_1, and a_2 as a function of h_2 for each series, and from these curves were constructed the more important sections of the thermodynamic adsorption surfaces of both components.

In each series of experiments the relative pressure of water h_2, remained practically constant and, therefore, the curves 1-5 on Fig. 2 are very close to the isobars h_2 = const. It follows from Fig. 2 that as the n-heptane adsorption, a_1 increases, there is observed in all cases first a small reduction in the water adsorption a_2, but with further increase in a_1 the water adsorption stops changing and remains constant, independently of the quantity of adsorbed heptane. Curve 4 of Fig. 2 shows especially clearly that at h_2 = const, n-heptane is not able to replace water adsorbed on silica gel, even at $h_1 = 1$. This curve ends at the point C, lying on the straight line AB, going through the points a^0_{s1} = 5.56 and a^0_{s2} = 48.5 millimole/g, lying on the coordinate axes and corresponding with the limiting values for the adsorption of heptane and water on the individual isotherms of Fig. 1. In the present case, both substances satisfy Gurvich's rule to an accuracy of approximately 1%, since the limiting adsorbed volume, determined for n-heptane, is v_s = 0.880, and for water is v_s = 0.892 cm^3/g. Therefore, the straight line AB corresponds with constancy of the sum of the volumes of both substances in the filled adsorption volume, and represents the boundary, to the right of which no experimental points can be found under the condition of additive volumes of both components in the adsorbed state. Since the point C, corresponding with the last experiment of series four, lay very accurately on the straight line AB, this means that in the present system additivity of volumes is maintained. In view of the fact that in series four the isotherms were carried right up to the limiting values a_1, we are able to evaluate the effect of

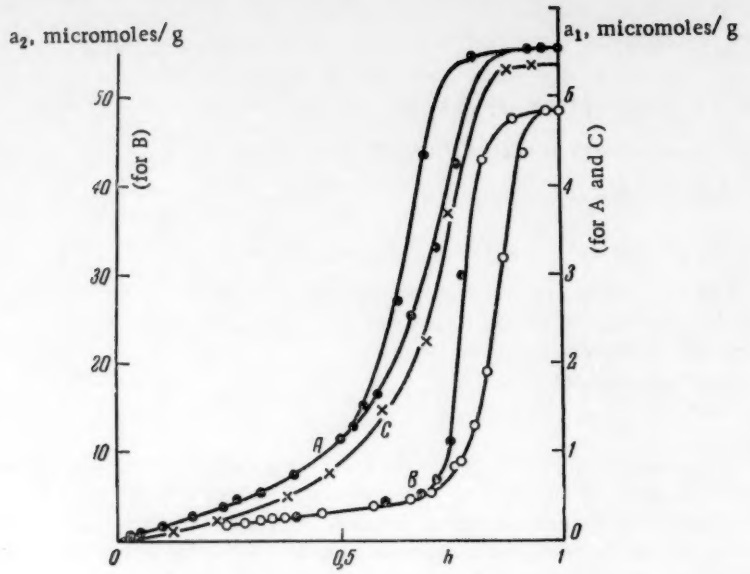

Fig. 1. Individual adsorption isotherms: A) n-heptane; B) water; C) adsorption isotherm of n-heptane in the presence of water.

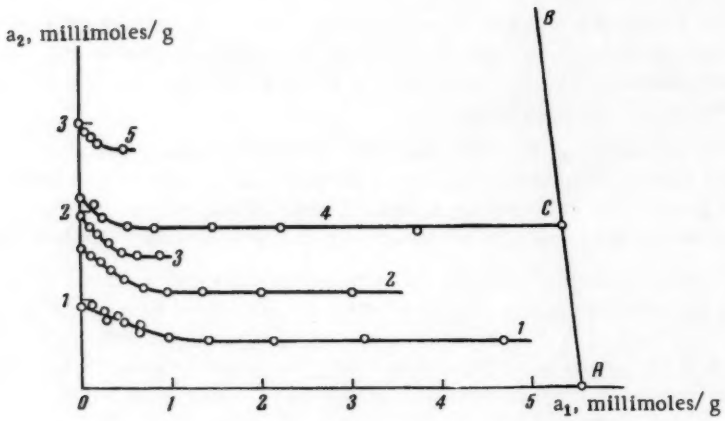

Fig. 2. Experimental data on the adsorption of vapor mixtures.

adsorbed water on heptane adsorption over the whole range of values of h_1. In Fig. 1, the adsorption isotherm of heptane at $h_2 \approx 0.31$ (curve C, corresponding with series four) is given for comparison with the individual heptane adsorption isotherm (curve A) over the whole region of variation of h_1. For values of h_1 from 0.4 to 1, the curve C also corresponds with the constant water adsorption $a_2 = 1.8$ millimole/ g, as may be shown by constructing the curves $a_2 = f(a_1)$ for series four. The isotherm C is very close in form to the isotherm A, and it likewise shows the characteristic property of being almost horizontal in the region of large h_1 values.

In analyzing the results of the experimental study of the adsorption of mixtures of water and n-heptane vapor on silica gel, it must be kept in mind that, in the present case, the purely adsorptive interaction of the two substances with the solid surface is complicated by polymolecular adsorption and temporary condensation of vapor in the spaces between the elementary silica gel particles. The individual isotherms of Fig. 1 testify to the fact that adsorption in the monomolecular region is only a small part of the total amount of sorption at h = 1, and that the principal part of the absorbed substances is sorbed by a polymolecular adsorption mechanism or by capillary condensation.

Unfortunately, a study of the hysteresis region in the case of mixtures of vapors of two substances turns out to be considerably more complicated than in the case of a single substance. The thing is that, if we do aid desorption by reducing the partial pressure of only one component (for example, by condensing part of the water in the apparatus), during the desorption of this component the adsorption of the other component is not reduced, but increased. Therefore, in an experiment of this sort, we get a desorption point for the one component and an adsorption point for the other component. Apparently, the only right way to do the experiment would be to remove a certain amount of strictly equilibrium vapor mixture from the apparatus, or to lower the pressure of the vapor by slowly increasing the volume of the system. Neither of these possibilities was provided for in our apparatus and, therefore, we were obliged to give up trying to study the desorption branches in the sorptional hysteresis region of the mixtures.

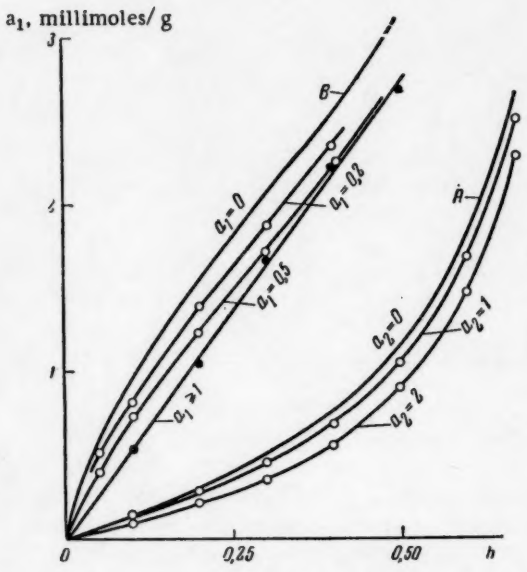

Fig. 3. Adsorption isotherms of one component with constant adsorption of the other component.

Going over now to the elucidation of the characteristic properties of the system being studied, we shall consider first of all the curve $a_1 = f_1(h_1)a_2$ shown in Fig. 3, i.e., the adsorption isotherms of n-heptane at constant values of water adsorption, and the curve $a_2 = f_2(h_2)a_1$, i.e., the adsorption isotherms of water at constant values of n-heptane adsorption. In Fig. 3, along with the individual n-heptane adsorption isotherm (curve A) are sketched the adsorption isotherms of heptane at $a_2 = 1$ and $a_2 = 2$ millimole/ g over a range of values of h_1 from 0 to 0.7. In examining these curves, our attention is called to the unexpectedly small reduction in n-heptane adsorption caused by adsorbed water. As was said above, the n-heptane adsorption isotherm for the range of h_1 from 0.1 to 0.4 is described by the BET equation with the constant $a_m = 0.99$ millimole/ g. The corresponding constant for water is $a_m = 2$ millimole/ g. If we start with the specific surface S = 380 m^2/ g, found from the adsorption of nitrogen vapor, and take the molecular area of heptane to be $\omega = 45A^2$, the capacity of the monolayer is $a_m = 1.37$ millimole/ g. It might be thought from this that the range of h_1 from 0 to 0.5 on the individual isotherm corresponds mainly with monomolecular heptane adsorption. If we admit that the surface of coarsely porous silica gel is relatively homogeneous, then at $a_2 = 1$ millimole/ g the degree of filling of the surface with water molecules is $\theta_2 \approx 0.5$. It would be expected that, for Langmuir adsorption of a mixture on a nonhomogeneous surface, for a fixed value of h_1, the relative lowering in the heptane adsorption $\Delta a_1 / a_1^0$ at $\theta_2 \approx 0.5$ would be equal to, or greater than 0.5 while, in fact, as follows from Fig. 3, it amounts to only about 0.1.

The form of the isotherm which we obtained for the adsorption of heptane on silica gel reminds us very much of the adsorption isotherms of isomeric hexanes on the surface of water, found in [4], by measuring the surface tension. From our point of view, this similarity is caused by the fact that, in both cases, we are dealing with rather similar adsorption mechanisms. The surface of hydrated silica gel is covered with hydroxyl groups and, therefore, as regards adsorption, it suggests the surface of water to a certain degree. The interaction energy of a hydrocarbon molecule with a homogeneous water (or silica gel) surface is not large, and induction effects are probably absent. Therefore, Van der Waals attraction forces play a relatively large role, acting between the adsorbed molecules, and causing the concavity of the isotherm in its initial region. At the same time, the adsorption of water on the surface of silica gel is, in all probability, localized, the adsorption centers in this case being the hydroxyl groups on the surface. The adsorption of water molecules on centers of this sort cannot cause any appreciable change in the adsorptive properties of the surface toward heptane molecules, since the surface is covered with hydroxyl groups to start with.

To explain the small magnitude of the relative lowering of heptane adsorption in the presence of water, it might be assumed that, for example at $a_2 = 2$ millimole/ g, the whole silica gel surface is uniformly covered with a monomolecular water layer, and that the heptane is adsorbed on this somewhat modified surface with a lowered adsorption potential. However, this idea of a uniform coating of the silica gel surface with adsorbed water molecules is not in accord with the facts. Somewhat later we shall present the considerations which contradict this assumption.

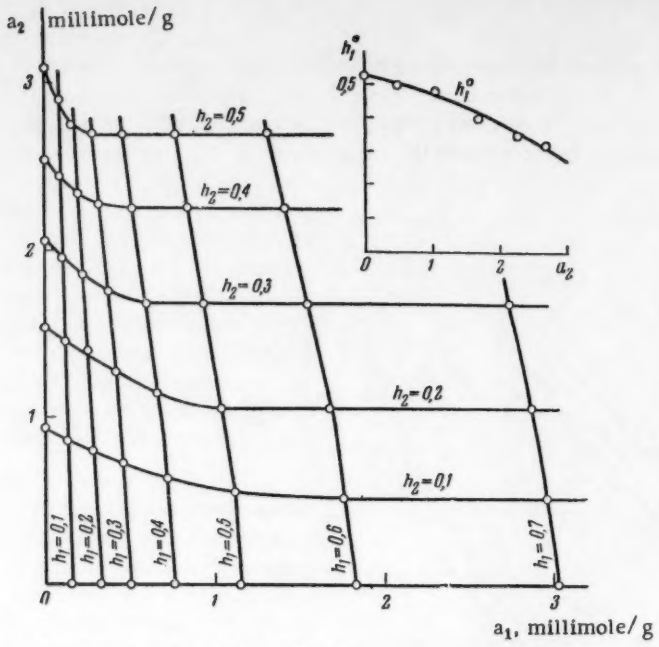

Fig. 4. Adsorption isobars of n-heptane and water.

It seems to us more nearly correct to assume that, in combined adsorption, even at very large filling, the water and heptane form a microheterogeneous system, and that subsequent heptane adsorption occurs principally on nuclei of the condensed heptane phase, formed on the parts of the surface with an elevated adsorption potential, for example in the zones of contact of the elementary silica gel particles.

Figure 3 also shows a family of water adsorption isotherms for constant amounts of adsorbed heptane equal to 0, 0.2, 0.5, and 1 millimole/g. Examination of these curves makes it possible to observe the relatively small effect which the adsorbed heptane has on the adsorbed water. Although the heptane capacity of the monolayer is $a_m \approx 1$ millimole/g, along the curve $a_1 = 0.5$ millimole/g the "degree of filling of the surface" by heptane is $\theta_1 \approx 0.5$. If all this heptane were uniformly distributed over the surface of the silica gel, we would expect that the water adsorption would be lowered by approximately 50%, while, as a matter of fact, the lowering amounts to only 15-18%. Thus, in the monomolecular surface filling range, both water and heptane interfere only slightly with one another's adsorption and, during adsorption on silica gel, there is comparatively weak competition, in contrast with the case of combined adsorption of these substances on activated charcoal. For $a_1 = 1$ millimole/g, the water adsorption isotherm in the region studied is practically a straight line passing through the origin of coordinates, further increase in a_1 having no effect on the water adsorption isotherm, since all the curves for $a_1 >$ > 1 millimole/g coincide with this straight line. Hence, it may be concluded that there is some part of the surface on which water alone is adsorbed. Heptane cannot replace water from this part of the surface even when it is adsorbed in large quantities.

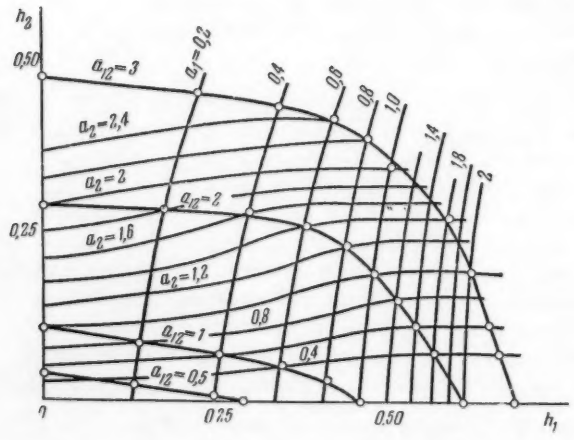

Fig. 5. Adsorption isosteres of n-heptane and water.

One is inclined to think that, in a similar way, some part of the silica gel surface would show increased activity toward heptane. It is possible to come to this conclusion from inspecting the water-adsorption isobars.

In Fig. 4, the heptane isobars h_1 = const are constructed in the coordinates a_1, a_2 for values of h_1 = 0.1, 0.2, ... 0.7, and the water isobars h_2 = const are constructed for values of h_2 = 0.1, 0.2, . . . , 0.5. These two families of isobars give a very compact graphic representation of the system being studied. Going along the water isobars, h_2 = = const for a gradual increase in h_1, the first thing that happens is a small reduction in water adsorption, amounting in all cases to about 0.4-0.5 millimole/ g, and then with further increase in h_1, replacement of water by heptane practically stops completely, and the isobars h_2 = const run parallel to the axis of abscissas. This picture is observed for all the isobars studied, and is in agreement with the experimental curves of Fig. 2. Thus, the first portions of heptane partially replace the water even at a_2 = 3 millimole/ g. This means that some part of the silica-gel surface exhibits an increased value of adsorption potential for heptane in comparison with the rest of the surface.

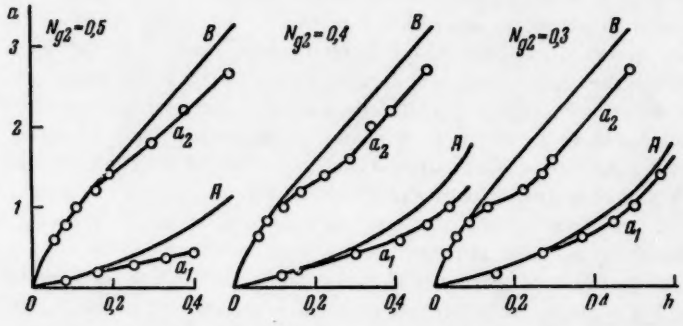

Fig. 6. Adsorption of n-heptane and water with constant composition of the gaseous phase.

The fact is worthy of consideration that as h_2 is increased, the horizontal parts of the isobars h_2 = const begin at lower heptane pressures. From our point of view, these horizontal segments, along which heptane adsorption occurs without replacing water, are caused by capillary condensation of heptane. We shall illustrate this point of view from the isobars h_2 = 0.5. In the absence of heptane vapor, the water adsorption at h_2 = 0.5 is equal to 3.1 millimole per g. As soon as heptane appears in the system, the molecules of this component are adsorbed on the parts of the surface with the largest values of adsorption potential, i.e., most probably in the spaces between the contacting silica-gel particles, and replace the water molecules from the surface of these localities. At h_1 = 0.3, approximately 0.4 millimole/ g of water is displaced, and approximately 0.3 millimole/ g of heptane is adsorbed. The adsorbed heptane forms nuclei of the condensed phase in the contact zones of the silica-gel particles. With subsequent increase in h_1, condensation of heptane vapor occurs on the liquid heptane meniscuses formed, this process having nothing to do with the replacement of water from the surface layer, since the adsorption potential on the surface of the liquid heptane meniscuses is higher than the adsorption potential of heptane on the main part of the surface. If this assumption is correct, and the occurrence of a horizontal segment in the isobars h_2 = const corresponds with the beginning of capillary condensation of heptane, one would expect a priori that, as a_2 increases, the beginning of the horizontal portion of the isobars would move to the left. Qualitatively, this is obvious. Actually, as a_2 increases, the mean thickness of the adsorbed water layer on the silica-gel surface increases. Therefore, the mean equivalent pore radius of the silica gel should fall off with increasing a_2, and the capillary condensation in the pores should begin at lower relative heptane pressures.

If, from the isobars of Fig. 4, we make an approximate determination of the value of h_1^0, corresponding with the beginning of the horizontal portion of the isobars h_2, and we plot h_1^0 as a function of the amount of water adsorbed, we find a systematic decrease in h_1^0 with increase in a_2, as is shown in the upper right-hand corner of Fig. 4 (curve h_1^0). For the point a_2 = 0 on the h_1^0 curve, a value of h_1^0 was taken, corresponding with the point where hysteresis starts on the individual adsorption isotherm of heptane.

On the basis of the h_1^0 curve of Fig. 4, we may come to the conclusion that, like heptane, the water is not distributed uniformly either over the silica-gel surface, at any rate during combined absorption of both substances. If the water is adsorbed in a quantity corresponding with the monolayer capacity, i.e., at a_2 = 2 millimole/ g, the value of h_1^0 is reduced from 0.53 to 0.40. From Kelvin's equation, the radius of curvature r of a spherical meniscus of a liquid with complete wetting is

$$r = -2\sigma v / RT \ln h, \quad (1)$$

where σ is the surface tension of the liquid, and $\underline{v}$ is its molar volume. If r_0 is the radius corresponding with the value $h_1^0 = 0.53$, and r_1 is the radius corresponding with the value $h_1^0 = 0.40$, then, from Eq. (1), $r_1 = 0.70 r_0$. At the same time, $r_0 = 26$A since, at 75°, $\sigma = 14.8$ dyne/cm, and $v = 157$ cm^3/mole. Hence, $r_1 = 18$A and, consequently, the thickness of the adsorbed water layer is equal to 8A. This value for the water monolayer is improbably large; therefore, one is inclined to think that the adsorbed water in the case under consideration covers the silica-gel surface nonuniformly and forms thicker layers in the finer pores. It follows from what has been said that, in the system under consideration, the adsorbed "solution" is microheterogeneous, even at comparatively small degrees of filling of the adsorptional volume.

Figure 5 shows the family of heptane adsorption isosteres a_1 = const for values of a_1 equal to 0.2, 0.4, . . . , 2 millimole/g, the family of water adsorption isosteres a_2 = const for values of a_2 equal to 0.4, 0.6, . . . , 2.4 millimole/g, and the family of total adsorption isosteres $a_1 + a_2 = a_{12}$ = const for values of a_{12} equal to 0.5, 1, 2, and 3 millimole/g. The a_1 isosteres on Fig. 5 differ from the corresponding isosteres for the less-adsorbed component in the system ethylene – propylene – charcoal [5] in that there is no slow rise in the initial portion and in the sign of the curvature. The a_2 isosteres in the region of small values of h_1 are very reminiscent of the corresponding isosteres for the more-adsorbed component in the system mentioned [5]. However, at large values of h_1, all similarity disappears, since the curves of Fig. 5 become practically parallel to the axis of abscissas. The a_{12} = const isosteres are typical of systems having limited mutual solubility of the two adsorbed substances in the liquid state, which are characterized by large positive deviations from Raoult's law. At small degrees of filling the a_{12} = const isosteres are almost linear, but as the parameter a_{12} increases, they become more and more convex and gradually approach the "right-angle" isosteres, characteristic of substances which are not soluble in one another. Like the isobar net of Fig. 4, the isostere net of Fig. 5 gives a very compact graphical representation of the system under study.

In conclusion, we shall consider the sections, corresponding with constant composition of the gaseous phase. Figure 6 shows three such sections, constructed for values of mole fraction of water N_{g2} in the gaseous phase equal to 0.5, 0.4, and 0.3. The curves A and B are the individual adsorption isotherms of heptane and water. The curves a_1, located below the curves A, represent heptane adsorption isotherms for N_{g2} = const, and the curves a_2, lying somewhat below the curves B, correspond with water adsorption isotherms for constant composition of the gaseous phase. The relative pressure h_1 and h_2 are plotted as abscissas.

If we gradually increase the pressure of the mixture of vapors having, for example, the composition $N_{g2} = 0.5$, over silica gel, at first the adsorption isotherms of heptane and water coincide with the corresponding individual isotherms A and B, i.e., the adsorption of each substance proceeds as though the other component were absent. On compressing the mixture further, a small reduction in adsorption of each component occurs as compared with the adsorption values on the A and B isotherms. If the parameter N_{g2} is reduced (i.e., the concentration of heptane in the gaseous phase is increased), the heptane adsorption isotherm a_1 approaches the curve A, the region of coincidence of the two curves broadening. At the same time, a noticeable reduction in the water adsorption is observed at all the lower pressures h_2. However, in all cases (including other values of N_{g2} not shown in Fig. 6), the initial region remains approximately independent of the adsorption of the two components. This fact gives evidence that the adsorption of water and n-heptane on silica gel in the monomolecular region occurs on different adsorption centers. As the parameter N_{g2} is reduced, a flex point appears on the water adsorption isotherm, and is gradually displaced in the direction of the origin of coordinates. This form of the a_2 curves is due to the existence of the limiting curve on Fig. 3 for $a_1 \geq 1$.

SUMMARY

1. The volume–weight method has been used at 75° to study the adsorption of mixtures of water and n-heptane vapor on silica gel, and the more important sections of the thermodynamic surfaces for the adsorption of both substances have been constructed.

2. In the monomolecular region, water and n-heptane exhibit unusually weak interference with one another's adsorption. In the initial region, the two substances are adsorbed practically independently of one another on different adsorption centers.

3. Even at small degrees of surface filling in the system studied there is no appreciable formation of a statistical two-dimensional solution of the two substances. Because of the inhomogeneity of the surface, the adsorbed "solution" is a microheterogeneous system. In the large sorption region capillary condensation of the two components occurs in different zones of the sorption volume.

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MECHANISM OF DEHYDROGENATION OF CYCLOHEXANE ON THE CRYSTALLINE α-OXIDE OF CHROMIUM

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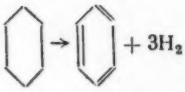
The dehydrogenation of hydrocarbons belonging to the cyclohexane series has been studied by many investigators, and a large amount of experimental material has been collected in this field. However, up to the present time, some questions relative to the reaction mechanism have remained unresolved. The views which have been advanced are as follows.

Sextet Mechanism. According to this mechanism, the cyclohexane molecule is adsorbed flat. Removal of the six hydrogen atoms occurs simultaneously in the sense that what is desorbed into the volume is benzene only, and not some intermediate form. Therefore, no cyclohexane is to be observed in the gaseous or liquid phase.

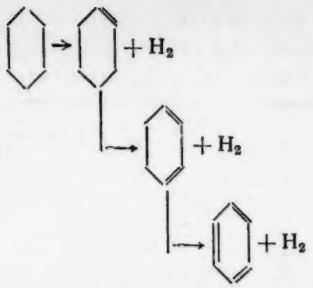


(1)

This mechanism has been proposed [1] for metallic catalysts with a cubic or hexagonal lattice and interatomic distances from 2.48A (Ni) to 2.77A (Pt). Confirmation of this mechanism has been found in [2-6]. The sextet mechanism for the dehydrogenation of cyclohexane on metallic catalysts is distinguished by the following features: a) the reaction takes place in the low-temperature range; b) activation energy is small; c) there is no cyclohexane in the reaction products. However, the sextet mechanism turns out to be unsatisfactory for explaining the way the reaction proceeds on some metals. This is shown, for example, in the papers of Balandin, Karpeiska, and Tolstopyatova [7,8], where the reaction proceeds according to the sextet mechanism with a ragnium catalyst on charcoal at low temperatures, while with the less active catalysts ragnium on Al_2O_3, and ragnium on asbestos at high temperatures, the doublet mechanism is the probable one.

Even earlier, Balandin and Brusov [9] pointed out that dehydrogenation of hydrocarbons, including ethane, on palladium at high temperature should take place according to the doublet mechanism. A sideways doublet orientation of the cyclohexane molecule is also possible in catalysis over a platinum catalyst at high pressure, since, at high temperature and pressure, the plane sextet orientation tries to go over into a sideways doublet orientation. This is found to have a theoretical explanation. As the temperature is increased, the molecular motion becomes stronger, and the cyclohexane ring comes to be fastened to the surface not by six, but by two carbon atoms, around which the molecule begins to oscillate. A similar fact was observed in our laboratory during studies on the adsorption of alcohols on aluminum oxide. As the temperature is raised, the orientation of the adsorbed molecules relative to the aluminum oxide surface changes from parallel to perpendicular, which is observable from the reduction in elementary area [10]. Raising the pressure in the system being dehydrated should also be accompanied by densification of the layer of adsorbed molecules. The latter, as a result of side forces, try to distribute themselves more compactly on the surface, as in the films on a liquid in Langmuir's experiments. This should also cause sideways orientation to predominate over the plane.

Doublet Mechanism. In this mechanism, the cyclohexane molecule is adsorbed lying on its side with the rupture of two C – H bonds. In this case, a crystalline catalyst is not required. In the dehydrogenation of cyclohexane, the hydrogen molecules are taken off in a definite order, forming cyclohexene, cyclohexadiene, and benzene:



(2)

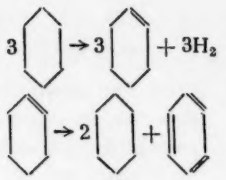
The sideways doublet mechanism for the dehydrogenation of the cyclohexane ring on oxide catalysts was first proposed in a paper by Balandin and Brusov [9]. It is distinguished by the following features: a) Cyclohexane dehydrogenation in a high range of temperatures; b) Large activation energy; c) Unsaturated hydrocarbons in the reaction products. The dehydrogenation kinetics of cyclohexane on chromium oxide has been studied in papers by Balandin and his co-workers [9, 11-13], as well as by a number of other authors [14-19].

It was shown that for catalysts prepared in different ways the activation energy ϵ of the reaction in question lies within the limits 13-41 kcal/mole. This difference in the values of the activation energy is apparently caused by the fact that, in some cases, the authors were dealing with x-ray amorphous chromium oxide, while in other cases they were dealing with the crystalline form. Rode [17] has described crystalline chromium oxide samples with ϵ = = 13.3 kcal/mole, while for amorphous samples, independently of the method of preparation, she found values of activation energy ϵ = 33.4 kcal/mole. In [18], a value of ϵ = 33.0 kcal/mole is also given for amorphous chromium oxide. One is obliged to feel that, carrying out the reaction in the high-temperature range and the high value of activation energy are characteristic only of amorphous chromium oxide.

Mechanism of Dehydrogenation of Cyclohexane Through Irreversible Catalysis. Kagan and his co-workers [20-24] have continued in their view that the first stage of the reaction consists in removing hydrogen from three molecules of cyclohexane to form cyclohexene and liberation of hydrogen into the volume. The cyclohexene, not being desorbed, undergo irreversible catalysis.

(a)

(b)



(3)

The authors adduce some arguments in favor of the mechanism in question which, however, are not satisfactory. In addition, as Kiperman has shown, the schemes offered for the mechanism are, in general, unsatisfactory from the point of view of the principle of detailed equilibrium.

Plate [25] has proposed that on a catalyst consisting of vanadium oxide on aluminum oxide there are two types of active centers: doublets, and sextets. In Davis's paper [26], it was shown that the structure of crystalline chromic oxide is such that a plane distribution of cyclohexane molecules on its surface is possible and, consequently, the reaction can proceed according to the sextet mechanism. Herrington and Rideal [15] consider that on a chromium aluminum catalyst the dehydrogenation of cyclohexane follows a sequential doublet scheme, with desorption of cyclohexane into the volume. Recently a paper appeared by Noller and Hantke [27], in which the dehydrogenation of cyclohexane to benzene on metals is considered to be a step process, since the heat of reaction (48 kcal/mole) is greater than the apparent activation energy (ϵ = 6-20 kcal/mole). On this basis, the authors mentioned reject the sextet mechanism. However, a stepwise reaction is not in contradiction with this mechanism. The sextet mechanism may occur in steps (compare [28]); the hydrogen may be split off from the cyclohexane molecule in a definite order, until the benzene is desorbed. Therefore, Noller and Hantke's objections do not refute the sextet mechanism.

EXPERIMENTAL

The chromium oxide catalyst used in the work was crystalline α-Cr_2O_3, as was shown by x-ray structure and electronographic methods. The initial materials, preparation of the catalysts, and the technique of carrying out the experiments are described in our previous paper [29].

TABLE 1. Cyclohexane Dehydrogenation on Chromium Oxide Catalyst (Catalyst volume 5 ml, material addition rate 0.167 ml/min, $\epsilon = 14.5$ kcal/mole, $k_0 = 0.4 \cdot 10^6$, $\epsilon / \log_{10} k_0 = 2.6$, $v_{0_{H_2}}$ is the quantity of hydrogen liberated in the reaction from 0.167 ml of cyclohexane, $m_{H_2} = v_{0_{H_2}}$, referred to one ml of catalyst)

Temp., °C	$v_{0_{H_2}}$, ml/min	m_{H_2}, ml/min · ml · cat	m_{H_2} calc. at $\epsilon = 14.5$ and $\log k_0 = 5.5557$	Cyclohexane, converted to benzene, %	
				from gas composition	from catalysate composition
335	11.13	2.23	2.21	10.7	10.5
347	14.17	2.83	2.79	13.7	–
368	18.63	3.73	4.10	18.0	17.5
376	22.77	4.55	4.41	22.0	22.0
395	32.77	6.55	6.49	31.6	31.5

The cyclohexane dehydrogenation on the catalyst sample in question was carried out over the temperature range 330-400° (Table 1). The activation energy was $\epsilon = 14.5$ kcal/mole; $\epsilon / \log_{10} k_0 = 2.6$ (Fig. 1).

Cyclohexene was not observed in the liquid reaction products (Rosenmund titration). A chromatogram also showed that only cyclohexane and benzene were present. The gaseous reaction products consisted of pure hydrogen. The activity of the catalyst was constant throughout the course of any given experiment, and on going from one experiment to another.

Experiments with cyclohexene showed that over the temperature range 210-350° irreversible catalysis occurs, inasmuch as, at the lower temperatures (210-250°), there is simultaneous hydration of cyclohexene to cyclohexane, while at temperatures of 280° and above there is dehydrogenation of cyclohexene to benzene. It was not possible to determine the activation energy of the irreversible catalysis, since the catalyst was not sufficiently stable in these experiments. It is interesting to note that in the experiments with cyclohexene, methylcyclopentane was observed in the liquid reaction products, the quantity of which increased with the temperature, as well as a small admixture of methylcyclopentene (Table 2). The results shown suggest that in the case investigated, plane orientation of the cyclohexane molecules occurs.

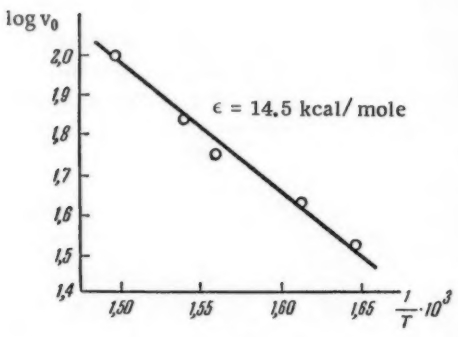


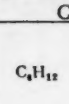
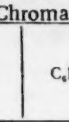
Fig. 1.

The results obtained are somewhat in contradiction with [9, 12]. However, the reason for this contradiction is obvious, since, in all probability, the authors were dealing with amorphous chromium oxide; the preliminary treatment with hydrogen at 450°, used in these papers, is insufficient to convert it to the crystalline state [17].

To confirm the assumption of a plane mechanism, some additional experiments were set up in collaboration with G. V. Isagulyants and Yu. I. Derebentsev, using tracer atoms, which will be described in a subsequent communication. The experiments were set up as follows. A mixture of labeled cyclohexane and unlabeled cyclohexene or unlabeled cyclohexane and labeled cyclohexene was passed over the catalyst. In the first case, the appearance of labeled atoms in the cyclohexene, and in the second case a reduction in the number of labeled atoms in the cyclohexene resulting from dilution, would show that cyclohexene is formed as an intermediate product, i.e., that there is a stepwise reaction scheme. In the opposite case, it must be assumed that the mechanism is plane or, more accurately, that the cyclohexane is converted into benzene on the surface of the catalyst without releasing any intermediate forms into the gaseous phase.

It was shown that, in the experiments with labeled cyclohexane, the only transfer of labeled atoms that was observed was in benzene. In the experiments with labeled cyclohexene, the radioactivity was not reduced. These results are in good agreement with one another and show that the dehydrogenation of cyclohexane to benzene occurs without intermediate formation of cyclohexene, desorbed into the volume. It is interesting to note that in [30] and [31], in studying the mechanism of the dehydrogenation of butane to divinyl on an oxide catalyst, the opposite picture was observed, i.e., the dehydrogenation goes in two stages, in that all the butylene formed from the butane is desorbed from the catalyst before any further reaction occurs.

TABLE 2. Conversion of Cyclohexene with Crystalline $\alpha - CrO_3$

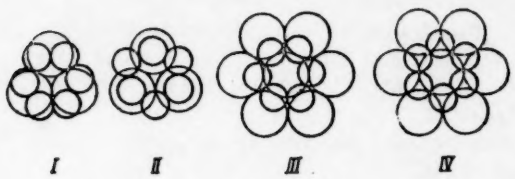
Temp., °C	v_{H_2}, ml/min	Chromatographic analysis of Catalysate**, %					
		C_6H_{12}	C_6H_6	C_6H_{10}	C_6H_{10}[1]		
209	0	8,9	1,6	89,0	88,3	0,6	
210	0	14,0	0,6	84,7	84,5	0,7	»
235	0	16,4	3,3	79,6	77,4	0,6	»
254	0	23,3	8,3	67,5	69,0	0,95	0
272	0	37,1	25,1	35,0	30,9	2,15	0
278	8.2	37,3	19,1	51,7	45,2	1,90	0
314	56,0	25,5	17,6	25,5	—	4,4	0
352	106,0	31,0	50,0	16,0	—	3,2	0

*Original cyclohexene contains 1.3% cyclohexane and 0.3% methyl cyclopentane.

** Analysis of catalyzate was performed by T. K. Lavrovskii on the chromatograph apparatus described in [34].

DISCUSSION OF EXPERIMENTAL RESULTS

It follows from the results of this work that the stepwise doublet mechanism of cyclohexane dehydrogenation accompanied by liberation of cyclohexene from the catalyst surface is not applicable to crystalline α-Cr_2O_3. Kagan's mechanism also drops out of the picture, since the schemes provided by this mechanism are in contradiction with the principles of detailed equilibrium and, consequently, are incorrect. The results obtained come closest of all to the plane sextet mechanism. Speaking in its favor, in addition to the results of the radiochemical study, are the results of the kinetic measurements which we found in the present paper: a) the reaction occurs in the low-temperature range; b) the activation has the small value ϵ = 14.5 kcal/mole; c) there is no cyclohexene in the reaction products; d) there is no methylcyclopentane in the catalyst, although it occurs in considerable quantities in experiments with cyclohexene; and e) the catalyst is stable in experiments with cyclohexane, and the catalyst is inactive in contact with cyclohexene. Nevertheless, the usual sextet mechanism, which occurs with metals, is not applicable here, since on Cr_2O_3 ($D5_1$ lattice) there are no faces, corresponding with the (111) faces of platinum and other metals with a type A 1 lattice, which actually showed the sextet mechanism (Fig. 2).



I II III IV

Fig. 2.

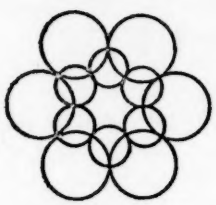


Fig. 3.

Crystalline α-Cr_2O_3 has an α-Al_2O_3-type structure. The oxygen atoms form an almost undistorted hexagonal close packing. The chromium atoms are in octahedral voids, and the chromium atoms are arranged in a layer according to the Corundum law in which two filled octahedral voids alternate with an unfilled one. Thus, on the surface of chromium oxide there are regular hexagons, consisting of chromium atoms, which form a network similar to the network of carbon atoms in the basopinacoid lattice of graphite, but with a larger interatomic distance, namely d = 2.83 A (according to V. M. Akimov's calculation). This value of d satisfies the requirements of the principle of conservation of valence angle of carbon atoms [32]. Thus, in α-Cr_2O_3, the chromium atoms form a face similar to the (111) face of platinum, but with regularly alternating vacancies.

In a paper by one of the authors [1], consideration was given to the ways in which a six-numbered ring may be located on the (111) face of an A 1 lattice and still maintain hexagonal symmetry. There are four such cases (see Fig. 2). Cases II and III are excluded because of the fact that these distributions of the carbon ring are sterically

hindered by the hydrogen atoms of cyclohexane, which may easily be seen if we construct models. Let us note that the model for case III of Fig. 2 is nothing but the model proposed by Trapnell as an improvement on the sextet model. From what has been said, it is clear that Trapnell's proposal is unacceptable.

Case I of Fig. 2 is the sextet model. There is no distribution of chromium atoms of this sort in the α-Cr_2O_3 lattice. As far as Case IV is concerned, it is possible here if we remove the central metal atom from the Case IV model, which corresponds with the vacancy that we spoke of above. Thus, the dehydrogenation of cyclohexane on crystalline chromium oxide is best described by the model shown in Fig. 3 of the present paper. This configuration provides for superposition on a hexagon of chromium atoms (d = 2.83 A) of a hexagon of carbon atoms from cyclohexane (d = 1.52 A) in such a way that the centers of both hexagons coincide, and the hexagons are rotated 30° with respect to one another in the plane of the drawing. The cyclohexane ring becomes plane under the influence of the adsorption forces. In the transition of cyclohexane from the trans form to the cis form as an intermediate form, the plane form must necessarily arise, and fastens itself onto the surface because of adsorption. In process of being torn off, the hydrogen atoms fall into the hollows between two chromium atoms, as in the model for dehydrogenation of open chains. It may be seen that the new model of the multiplet active complex (Fig. 3) for the dehydrogenation of hexahydroaromatic compounds on crystalline oxides of α-Cr_2O_3 type fits both the results of the kinetic and radiochemical study, and the structural peculiarities of these molecules and α-Cr_2O_3.

SUMMARY

Dehydrogenation of cyclohexane on crystalline α-Cr_2O_3 proceeds according to a sextet-type mechanism. This conclusion agrees with the structural principles of multiplet theory.

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STUDY OF THE ELECTROPHILIC SUBSTITUTION REACTION AT AN OLEFINE CARBON ATOM

COMMUNICATION I. REACTION OF TRANS-β-CHLORVINYLMERCURY CHLORIDE WITH IODINE IN THE PRESENCE OF IODINE ANION IN AQUEOUS DIOXANE

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The stereochemistry of electrophilic and homolytic substitution at an olefine carbon atom has been studied in detail by Nesmeyanov and his co-workers [1]. As a result of these studies a rule was formulated, called "Nesmeyanov and Borisov's rule" in the literature, to the effect that geometric configuration is rigorously maintained in reactions of the type under discussion. However, up to the present time, the kinetics of these reactions have not been studied, which makes it difficult to decide what the nature of the elementary act is.

In the present paper, we are beginning a study of the kinetics of electrophilic substitution at an ethylene carbon atom, effected by a halogen, as well as a study of the effect of the solvent on the reaction rate using, in the first instance, the reaction of trans-β-chlorvinylmercury chloride with iodine in dioxane.

$$Cl-CH=CH-HgCl + I_2(CdI_2) \xrightarrow{85\%\ \text{Aqueous Dioxane}} Cl-CH=CH-I + HgClI(CdI_2)$$

It is well-known that the reaction of alkylmercury halides, as well as 4-camphylmercury chloride with iodine in dioxane goes according to a radical mechanism. In the presence of an excess of lithium iodide in aqueous dioxane this same reaction goes according to an electrophilic mechanism, as proposed by the authors, through the following transitional state (A):

$$RHgX + I_2(\bar{I}) \longrightarrow \underset{\underset{I\cdots I}{\vdots}}{\overset{I}{\vdots}}\!\!R\cdots Hg-X \longrightarrow RI + HgXI(\bar{I})$$

(A)

As the source of halogen ions, we used cadmium iodide, since the iodides of monovalent metals react with the initial mercuroorganic compound. The fact that there are no reactions between cadmium iodide and the initial Biginelli compound during the interval of time in which the electrophilic substitution is taking place was demonstrated by special auxiliary experiments in which the cadmium iodide was titrated out quantitatively with mercuric chloride.

The reaction rate of trans-β-chlorvinylmercury chloride with iodine in excess cadmium iodide was measured in 85% aqueous dioxane. The kinetic measurements were made by the colorimetric method on an FÉK apparatus with a green filter. The reaction was carried out with equimolecular concentration ratios of the reacting substances, equal to $0.5 \cdot 10^{-3}$ and $1 \cdot 10^{-3}$ mole/liter, and cadmium iodide concentrations equal, respectively, to $0.5 \cdot 10^{-2}$ and $1 \cdot 10^{-2}$ mole/liter. The Lambert-Beer law was applicable to the solutions. Figure 1 gives the linear relation between the optical density and the initial iodine concentration in cadmium iodide solutions $d = f(c)$, in 85% aqueous dioxane.

EXPERIMENTAL

The dioxane was purified by the method described in [3]. To the dioxane solution of trans-β-chlorvinylmercury chloride in a thermostat was added a solution, previously held at the same temperature, of iodine and cadmium

TABLE 1.

$c_{0RHgX} = c_{0I_2} = 1 \cdot 10^{-3}$ mole per liter; $c_{0CdI_2} = 1 \cdot 10^{-2}$ mole/liter		$c_{0RHgX} = c_{0I_2} = 0.5 \cdot 10^{-3}$ mole/liter; $c_{0CdI_2} = 0.5 \cdot 10^{-2}$ mole/liter	
τ. sec	d	τ. sec	d
0	1,350	0	0,730
100	1,250	60	0,705
160	1,200	360	0,635
240	1,130	540	0,590
360	1,040	720	0,570
760	0,860	1080	0,520
1020	0,755	1440	0,480
1380	0,670	1800	0,445
1500	0,630	2160	0,410
1740	0,596	2460	0,390
1800	0,575	2980	0,350
2160	0,530	3600	0,320

TABLE 2.

$c_0 \cdot 10^3$, mole/liter	$\tau_{\frac{1}{2}}$, sec.	K_2, liter/mole·sec
1	1350	0.740
0.5	2850	0.710

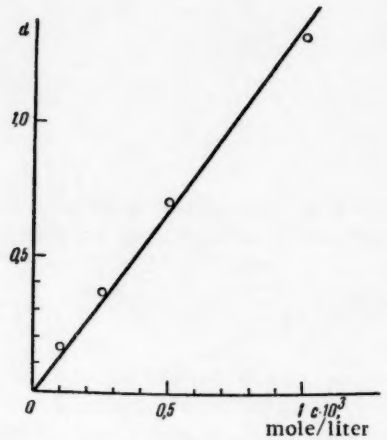

Fig. 1. The linear relation between the optical density and initial iodine concentration in cadmium iodide solutions $d = f(c)$, in 85% aqueous dioxane.

iodide in aqueous dioxane so as to give 85% dioxane in the final result. The moment the second reagent was added was taken as the beginning of the reaction. After a definite interval of time, a sample of the solution was taken out of the vessel, and a measurement was made of the optical density. Table 1 gives the experimental data on the variation of optical density with time for the initial reagent concentrations used at 20°.

The data of Table 1 were used to construct a curve of $(d_0 - d)/d$ against τ (Fig. 2) for the various reagent concentrations.

The linear form of the curve of $(d_0 - d)/d = f(\tau)$ shows the overall second order of the reaction and the consistency in the values of the constants K_2. From the curve of Fig. 2, mean graphic values of the half-exchange periods were found, which were used to calculate the rate constants of the second-order reaction (Table 2)

$$K_2 = \frac{1}{c_0 \cdot \tau_{1/2}}$$

To determine the order of the reaction for each of the components, the reaction kinetics were measured with a large excess of mercuroorganic compound (otherwise, the conditions under which the reaction was carried out were kept the same as before). Experimental data is given in Table 3. The data of Table 3 was used to construct a curve of $\log_{10}(d_0/d) = f(\tau)$ (Fig. 3) for different initial reagent concentrations. The linear form of $\log_{10}(d_0/d)$ as a function of τ shows that the reaction is first-order with respect to iodine. The reaction under consideration is of first-order with respect to iodine and, consequently is of first-order with respect to the mercuroorganic compound.

TABLE 3.

$c_{0RHgX} = 0.5 \cdot 10^{-2}$ mole/liter; $c_{0I_2} = 0.5 \cdot 10^{-3}$ mole/liter; $c_{0CdI_2} = 0.5 \cdot 10^{-2}$ mole/liter		$c_{0RhgX} = 1 \cdot 10^{-3}$ mole/liter; $c_{0I_2} = 1 \cdot 10^{-4}$ mole/liter; $c_{0CdI_2} = 1 \cdot 10^{-3}$ mole/liter	
τ. sec	d	τ. sec	d
0	0,730	0	0,163
7	0,520	7	0,123
17	0,300	17	0,070
30	0,140	25	0,045
		30	0,031

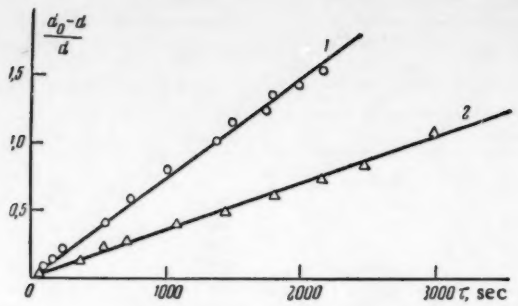

Fig. 2. Graphs for various initial concentrations of reagents: 1) $C_0 = 1 \cdot 10^{-3}$ mole/liter; 2) $C_0 = 0.5 \cdot 10^{-3}$ mole/liter.

TABLE 4.

15°		20°		25°	
τ, sec	d	τ, sec	d	τ, sec	d
0	1,350	0	1,350	0	1,350
45	1,310	100	1,245	180	1,100
90	1,290	160	1,200	306	0,990
180	1.230	240	1,120	378	0,940
270	1,195	360	1,040	540	0,820
360	1,130	760	0,860	675	0,750
900	0,930	1020	0,755	795	0,690
1080	0,860	1380	0,670	1080	0,590
1440	0,780	1500	0,630	1260	0,540
2160	0,640	1740	0,596		
2700	0,560	1800	0,575		
		1980	0,550		
		2160	0,530		

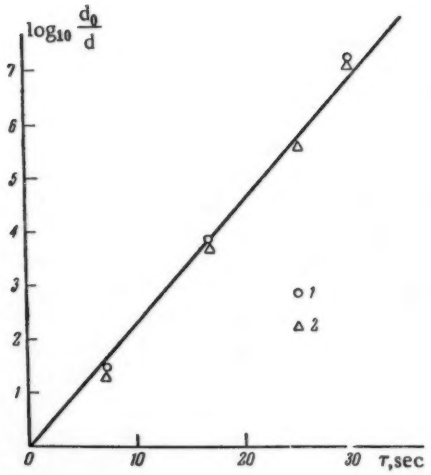

Fig. 3. Curve of $\log_{10}(d_0/d) = f(\tau)$ for the pseudomonomolecular reaction: 1) $c_{0RHgX} = 0.5 \cdot 10^{-2}$ mole/liter; $c_{0I_2} = 0.5 \cdot 10^{-3}$ mole/liter; 2) $c_{0RHgX} = 1 \cdot 10^{-3}$ mole/liter, $c_{0I_2} = 1 \cdot 10^{-4}$ mole/liter.

From the graphically averaged value of the half-exchange period, the rate constant of the pseudomonomolecular reaction was determined.

$$K_1 = \frac{0,693}{\tau_{1/2}} = 8,25 \cdot 10^{-2} \text{ sec}^{-1},$$

The reaction kinetics at the temperatures 10, 20, and 25° were measured for concentrations of the mercuroorganic compound and iodine equal to $1 \cdot 10^{-3}$ mole/liter, and a concentration of cadmium iodide equal to $1 \cdot 10^{-2}$ mole/liter. The change in optical density with time is given for the temperatures in question in Table 4.

Curves of $(d_0 - d)/d$ against τ are given for all temperatures in Fig. 4.

The second-order rate constants at temperatures 15, 20, and 25° were found from the graphically averaged values of the half-exchange periods. The values of the half-exchange periods, the reaction rate constants, their logarithms, the corresponding absolute temperatures, and their reciprocals are given in Table 5.

The logarithm of the reaction rate constant as a function of the reciprocal of the temperature is given in Fig. 5. The curve of $\log_{10} K_2 = f(1/T)$ gave the following parameters in the Arrhenius equation: E = 13.6 kcal/mole, $\log_{10} A = 10.0$, and activation entropy $\Delta S = -12.8$ entropy units at 25°.

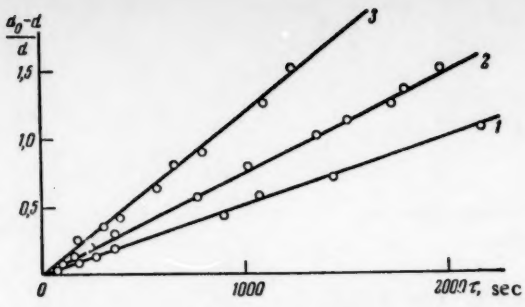

Fig. 4. Curve of $(d_0 - d)/d = f(\tau)$ for various temperatures: 1) 15°; 2) 20°; 3) 25°.

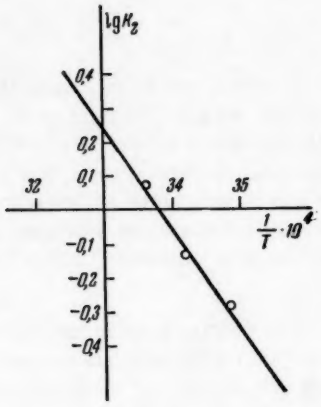

Fig. 5. Logarithm of the second-order constant as a function of the reciprocal of the absolute temperature.

TABLE 5.

T, °K	$\tau_{\frac{1}{2}}$, sec.	K_2, liter/mole · sec	log K_2	$\frac{1}{T}(10^4)$
288	1940	0.516	−0.288	34.8
293	1340	0.746	−0.127	34.2
298	840	1.190	0.076	33.6

A study was made of the stereochemistry of the reaction of trans-β-chlorvinylmercury chloride with iodine in excess cadmium iodide in 80% aqueous dioxane. To 3 g (0.0101 mole) of Biginelli compound in 25 ml dioxane was added a solution of 2.6 g (0.0102 mole) iodine and 3.66 g (0.1 mole) CdI_2. After disappearance of the iodine color, the dioxane was distilled off from a flask provided with a deflegmator. The residue was filtered off from the precipitate of HgClI + CdI_2, and the precipitate was washed on the filter with petroleum ether. After distilling off the petroleum ether, the residue was fractionated on a microcolumn. The yield was 0.92 g trans-1,2-chloriodoethylene (49% of the theoretical) with b.p. 110-112°, and $n^{15}D$ 1.5702. The data in the literature are: trans-chloriodoethylene, b.p. 113-114°, and $n^{15}D$ 1.5714; cis-chloriodoethylene, b.p. 116-117°, $n^{15}D$ 1.5828 [4].

SUMMARY

1. A study has been made of the reaction of trans-β-chlorvinylmercury chloride with iodine in excess cadmium iodide in 85% dioxane.

2. The over-all order of the reaction is equal to two. It is first-order for each of the components. The rate constants of the second-order reaction have been determined at various temperatures.

3. The following parameters have been found for the Arrhenius equation: E = 13.6 kcal/mole, $\log_{10}A = 10.0$, and activation entropy $\Delta S = -12.8$ entropy units at 25°.

4. A study has been made of the stereochemistry of the reaction. Under the conditions used, the reaction proceeds with strict conservation of configuration.

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THE LAWS GOVERNING THE EFFECT OF INHIBITORS IN THE OXIDATION OF POLYPROPYLENE

Paper presented at the General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, Moscow, June 22, 1961

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Many organic products, in particular lubricating oils and polymeric materials, are, in the course of use or treatment, subject to the action of high temperatures in the presence of atmospheric oxygen. To increase the stability of materials of this sort toward thermooxidational destruction, use is made of additions of antioxidants and oxidation inhibitors, usually phenols, aromatic amines, sulfides, phosphoric acid esters, etc. [1]. However, the theory of the action of oxidation inhibitors has been very unsatisfactorily worked out, and lags far behind the achievements and requirements of practice. In particular, the existing theoretical concepts require a linear relation between the induction period in the inhibitor concentration, at least at concentrations exceeding some minimum "critical" value [2-4], while for the most part no such relationship is fulfilled in practice [5-8].

We have studied the oxidation of linear isotactic polypropylene above its melting point in the presence of inhibitors such as p-phenylenediamine derivatives and alkylphenols. Here, in addition to the relation between the induction period and the inhibitor concentration and the temperature, a study was made of the change in inhibitor concentration with time in the induction period. To this end, a technique was worked out for quantitative distillation of unconsumed inhibitor out of the polypropylene sample, followed by a spectrophotometric determination. Experiments have shown that an inhibitor with a molecular weight of ~300 is practically completely distilled out of a 50-mg sample of melted polypropylene on the bottom of a vessel ~1 cm in diameter in vacuum at 200°C after 30 minutes. The technique of measuring the oxidation-induction periods was described in one of our previous papers [9].

The most detailed study was made of the oxidation of polypropylene in the presence of the alkylphenols: 2,6-di-(1,1-dimethylhexyl)-4-methylphenol (I) [10], and 2,2'-methylene-bis-(4-methyl-6-tert.butylphenol) (II). The experiments have shown that the monophenol (I) lengthens the induction period of polypropylene oxidation (Fig. 1, Curve 1) by an insignificant amount at 200° and 300 mm oxygen pressure, even in large concentrations, although at lower temperatures the effectiveness of this substance is markedly enhanced (Fig. 1, Curve 2). The biphenol (II) (Fig. 1, Curve 3) is considerably more effective, and the nature of the relation between the induction period in the concentration is markedly different for mono- and biphenol [(I) and (II)]. It is interesting that adding inhibitor (I) to polypropylene containing inhibitor (II) produces pronounced shortening of the induction period for polypropylene oxidation, although the total amount of inhibitor in the sample is increased (Fig. 1, Curves 4 and 5). The same effect is produced by adding α-naphthol. The induction period for polypropylene oxidation in the presence of phenols is strongly dependent on the oxygen pressure, and drops off rapidly with increase in pressure.

Figure 2 shows the curve of change in concentration in the inhibitors (I) and (II) in the induction period. The consumption of inhibitor (I) was observed at 180°, since this inhibitor is consumed too rapidly at 200°. It may be seen from Fig. 2 that, while (II) is consumed according to a first-order law as long as the concentration exceeds critical (effective rate constant equal to $1.9 \cdot 10^{-4}$ sec^{-1}), the concentration of (I) varies according to a more complicated law. Experiments with different initial concentrations of (I) and (II) have shown that the rate of inhibitor consumption may, to a first approximation, be considered a function of its concentration alone (at constant temperature and oxygen pressure). It may also be seen from Fig. 2 that, even with inhibitors having a molecular weight of about 300, about 10% of the inhibitor evaporates out of the sample being oxidized under our experimental conditions.

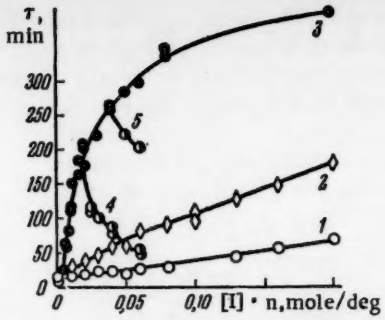

Fig. 1. Induction period of polypropylene oxidation as a function of phenol concentration: 1) inhibitor (I), 200°; 2) inhibitor (I), 180°; 3) inhibitor (II), 200°; 4) mixture of 0.1 mole/kg of (II) with a variable amount of (I); 5) mixture of 0.02 mole/kg of (II) with (I), 200°. The abscissas are the concentration of phenol groups, i.e., the product of inhibitor concentration by the number "n" of phenol groups in the molecule.

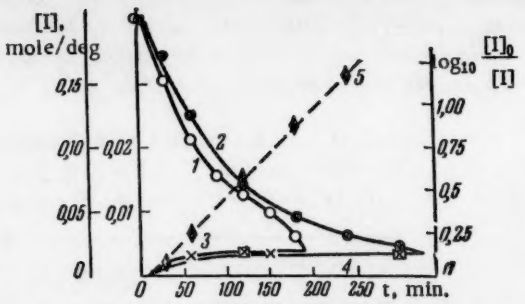

Fig. 2. Change in concentration of inhibitor (I) (Curve 1, left-hand scale) and (II) (Curve 2, right-hand scale), in the induction period of polypropylene oxidation. The curves 3 [inhibitor (I)] and 4 [inhibitor (II)] are the change in amount of inhibitor, distilled off in the course of the experiment onto the walls of the reaction vessel. 5 is the difference between Curves 2 and 4 with $\log_{10}[I]_0/[I]$ plotted against time. Temperature 180° for experiments with (I), and 200° for (II). P_{O_2} = 300 mm.

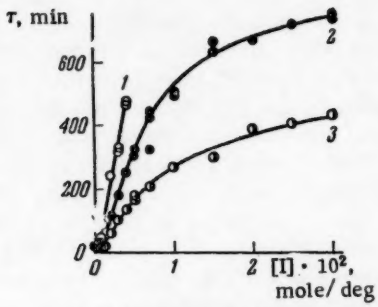

Fig. 3. Induction period for the oxidation of polypropylene as a function of the concentration of N-phenyl-N'-cyclohexyl-p-phenylenediamine (IV): 1) at 190°; 2) 200°; 3) 210°. P_{O_2} = = 300 mm.

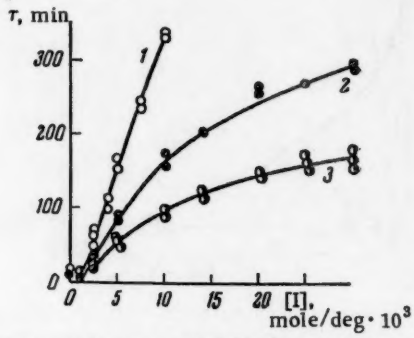

Fig. 4. Induction period for the oxidation of polypropylene as the function of the concentration NN'-dicyclohexyl-p-phenylenediamine (V): 1) at 190°; 2) 200°; 3) 210°. P_{O_2} = 300 mm.

We have also studied the oxidation of polypropylene in the presence of NN'-di-phenyl-p-phenylenediamine (III), N-phenyl-N'-cyclohexyl-p-phenylenediamine (IV), and NN'-dicyclohexyl-p-phenylenediamine (V). In the case of (III), we were not able to represent the experimental relationship between the induction period and the inhibitor concentration in the form of a continuous curve. Up to 0.01 mole/kg, (III) has almost no effect on the induction period, from 0.01 to 0.05 mole/kg a large spread is observed (from several minutes to 5 hr), above 0.015 mole/kg, the induction period changes very little with concentration, and amounts to about 5 hr.

Replacing one of the phenyl groups in (III) with cyclohexyl causes simultaneous subreduction in the critical concentration and lengthening of the induction period (Fig. 3). The curves of induction period as a function of concentration for an inhibitor like N-phenyl-N'-cyclohexyl-p-phenylenediamine (IV) are similar in form to the analogous curves for biphenol (II). In length of induction period (τ = 12.5 hr at 200°, P_{O_2} = 300 mm), (IV) exceeds both diphenyl-p-phenylenediamine (III), and NN'-dicyclohexyl-p-phenylenediamine (V) (Fig. 4). Figure 5 shows the changes in concentration of (IV) and (V) in the polypropylene being oxidized during the induction period. The form of these curves suggests the consumption curves of biphenol, and likewise they transform into straight lines when $\log_{10}[I]_0/[I]$ is plotted against time, i.e., (IV) and (V) are consumed according to a first-order law with the effective

constants $9 \cdot 10^{-5}$ sec^{-1} for (IV) and $1 \cdot 10^{-3}$ sec^{-1} for (V). In the case of (V), the initial inhibitor is practically all used up approximately after the first half of the induction period, after which the reaction is retarded by its transformation products. Retardation of the reaction by nonvolatile products of inhibitor transformation have also been observed in the case of inhibitor (IV). At the end of the induction period, these products disappear, too (see table).

Second Induction Period for the Oxidation of Polypropylene, Stabilized with (IV) and (V) as a Function of the Length of Original Oxidation (After the first oxidation the unconsumed inhibitor was removed. Temperature 200°, p_{O_2} = 300 mm Hg, $[I]_0$ = 0.03 mole/kg)

Oxidation time, min.	0	30	60	120	240	360	480	600	648
Second induction period, min, for (IV)	11	111	117	91	64	53	33,5	25	15
The same, for (V)	—	69	113	90	23	—	—	—	—

The amines (IV) and (V) are easily oxidized by oxygen. In particular, this explains the form of the inhibitor evaporation curves in Fig. 5. The inhibitor, which distills over onto the walls of the reaction vessel, which are heated, but not to 200°, is gradually oxidized, as a result of which the curves, showing the quantity of inhibitor on the vessel walls (Fig. 5, Curves 3 and 4), go through a maximum. The inhibitor (V) has a perceptible oxidation rate even at room temperature.

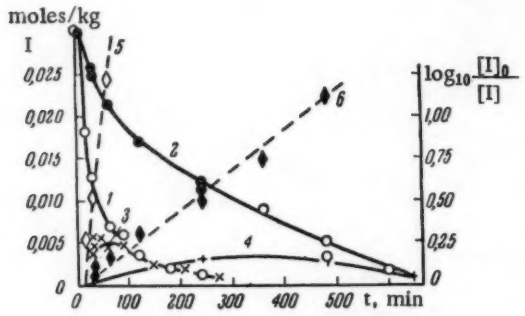

Fig. 5. Change in concentration of inhibitors (IV) and (V) in the induction period. 1 (V) and 2 (IV) are total amount of inhibitor; 3 (V) and 4 (IV) are amount of inhibitor on the walls; 5 (V), and 6 (IV) are amount of inhibitor in the polypropylene sample (difference between Curves 1 and 3, as well as between 2 and 4). Plot of $\log_{10}[I]_0/[I]$ against time at 200°, p_{O_2} = 300 mm.

Comparing the results obtained (first-order inhibitor consumption at large concentrations, induction periods strongly dependent on pressure), we came to the conclusion that the inhibitors (II), (IV), and (V) are consumed principally by direct oxidation and the secondary processes connected with it. Inhibitor oxidation also initiates oxidation of the polymer itself. Molecular weight determinations have shown that, for every five molecules of inhibitor (II) consumed, there is one rupture of a polymer chain, in experiments in which the initial concentrations and, consequently, the rates of consumption of (II), were widely different. These results are confirmed by the data from spectrum analysis. In the oxidation of polypropylene, stabilized with (II), a product appears, the spectrum of which coincides with the spectrum of the oxidation products of the polymer, and the quantity of which is proportional to the amount of inhibitor used up. In the case of (V), small concentrations of this easily oxidized inhibitor shorten the induction period for the oxidation of polypropylene.

The idea that the relation between induction period and inhibitor concentration fails to be linear at high concentrations because of oxidation of the inhibitor has been expressed previously [11,12]. We have also suggested that the inhibitor can take part in degenerate chain branching. Two active free radicals are formed at one and the same place, in one "cell," so to speak, during decomposition of one molecule of a branching product, for example a hydroperoxide, in a liquid or solid hydrocarbon medium. Recombination of these radicals into the original product can be reflected only in the rate, but not in the results, of the reaction. However, if one of the free radicals undergoes a reaction with a hydrocarbon molecule, located in the same "cell," the free hydrocarbon radical formed can recombine with the second radical to form a stable product, for example

$$\begin{aligned} &ROOH \rightarrow RO\cdot + \cdot OH \\ &R'H + OH \rightarrow R'\cdot + H_2O \\ &R'\cdot + RO\cdot \rightarrow R'OR \end{aligned} \qquad (1)$$

The fact that reactions of this sort can occur leads to the condition that the branching probability of a reaction involving decomposition of the hydroperoxide molecule is considerably less than one. If, however, in the one "cell," along with the hydroperoxide molecule, there is a molecule of the substance which is capable of undergoing reaction with only one free radical, the recombination probability is reduced, and the chain-branching probability is increased since, after the destruction of the one radical, the second radical will have nothing with which to recombine. Phenols are the nearest thing to a substance of this sort: after removal of hydrogen from the phenol molecule according to a reaction such as

$$ArOH + \cdot OH \rightarrow ArO\cdot + H_2O, \qquad (2)$$

a radical is formed of such a sort that, if $RO^{\cdot}$ is united with it at the place where the hydrogen atom was, what is formed is an unstable peroxide with the peroxide group in the aromatic nucleus, and the union of $RO^{\cdot}$ in the para position is prevented by the large dimensions of the phenol molecule. Here, the monophenol (I) will stimulate branching of the chains considerably more strongly than the biphenol (II), one molecule of which is capable of annihilating twice as many free radicals. This, apparently, is sufficient to explain the difference in action of the two related phenols (I) and (II), as well as the acceleration in the consumption of (II) in the presence of (I) or α-naphthol.

Thus, the greater part of the inhibitor is consumed in oxidation reactions by processes of this sort, and only a small part is consumed in pulling off chains, in the initiation of which the inhibitor takes no part. With a certain amount of simplification it can be said that an inhibitor of the type of biphenol (II) or of an aromatic amine, which is a weak chain-branching stimulator, is oxidized comparatively slowly at a concentration above critical with a rate $w_{0i} = k_i[I]$ until its concentration becomes equal to critical, after which an autoaccelerating process of oxidation of the polymer begins, which has an induction period τ_{cr}. This simplified picture gives the following relation between the induction period and the initial inhibitor concentration

$$\tau = \tau_{cr} + \frac{1}{k_i} \ln \frac{[I]}{[I]_{cr}}, \qquad (3)$$

where $[I]_{cr}$ is the critical inhibitor concentration.

Equation (3), to a first approximation, correctly describes the experimental dependents of τ on [I] for inhibitors of this type. Since both k_i and $[I]_{cr}$ are bound up with the mobility of one and the same phenol or amine hydrogen atom, a large value of k_i should correspond with a small value of $[I]_{cr}$ and the other way around. Apparently, in the better present-day inhibitors, the reactivity of the weakly bound hydrogen atom is close to optimum, and to make any substantial increase in the lifetime of the polymer at high temperatures it is necessary either to "stabilize" the inhibitor itself, i.e., reduce the value of k_i in one way or another, or to make a substantial reduction in the "critical" concentration value. Both these things can be accomplished by introducing into the polymer, in place of a single amine or phenol inhibitor, mixtures containing various special additives in addition to the basic inhibitor. In particular, the "critical" concentration may be lowered by using substances which destroy the hydroperoxides without forming free radicals.

SUMMARY

1. A study has been made of the oxidation of isotactic polypropylene, containing as inhibitors additives of aromatic amines or alkylphenols.

2. In the oxidation of polypropylene, the greater part of the inhibitor is consumed by direct oxidation and, in secondary processes related to it. Oxidation of the inhibitor also induces destruction of the polymer.

3. In the oxidation reactions, the inhibitor can apparently take part in the degenerate chain-branching act.

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THE DETERMINATION OF THE RATE CONSTANTS OF THE SIMPLE REACTIONS OF HYDROGEN ATOMS

COMMUNICATION 1. THE RATE CONSTANT FOR THE RECOMBINATION OF $H + H + H_2 \rightarrow 2H_2$ AND THE RATE CONSTANT FOR THE REACTION $H + O_2 + H_2 \rightarrow HO_2 + H_2$

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The rate constant of the reaction which produces the radical HO_2 from hydrogen atoms and oxygen molecules in the triple collision $H + O_2 + M \rightarrow HO_2 + M$, where M is a molecule of hydrogen, has been determined previously by other authors [1-3]. The three values of the constant which were obtained do not agree among themselves; the minimum value [1] differs from the maximum [2] by two orders of magnitude. The rate constant for hydrogen-atom recombination in a triple collision also has been determined previously by a number of authors [1,4-6]. These values are in good agreement with one another. The present work was begun for the purpose of measuring the rate constant of the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$, based on a method which we suggested for the measurement of the rate constants of reactions of atoms and radicals [7].

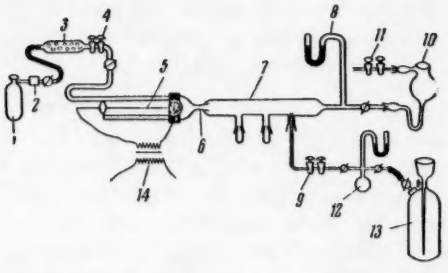

Fig. 1. Scheme of apparatus: 1) hydrogen cylinder; 2) special valve; 3) $CaCl_2$ tube; 4), 9), 11) stopcock valve; 5) ozonizer-type tube; 6) nozzle; 7) reaction vessel; 8) manometer for measuring pressure in reaction vessel; 10) removable trap; 12) calibrated vessel from which O_2 is supplied to reaction vessel; 13) gas-meter for O_2.

EXPERIMENTAL

The experiments were carried out in a flow system in the glass vacuum apparatus which is shown schematically in Fig. 1. The source of hydrogen atoms was a silent discharge in an apparatus like an ozonizer. A high-voltage transformer of 40,000 volts was used for the discharge. The ozonizer was connected to the reaction vessel by a fine nozzle. The nozzle between the discharge zone and the reaction vessel guaranteed the impossibility of the diffusion of O_2 molecules into the discharge zone when oxygen molecules were admitted to the jet which contained the hydrogen atoms. The reaction vessel had a diameter of 20 mm and a length of 1.2 m. The electrolytically produced molecular hydrogen used for these experiments was kept in an ordinary cylinder. The cylinder was connected to the apparatus with a special valve similar to the valves used in aqualungs for underwater swimming; it made possible a constant atmospheric pressure of hydrogen. A calcium chloride tube was placed between the valve and the glass part of the apparatus for the removal of the water vapor and oil which escaped with the hydrogen from the cylinder. A removable trap, cooled with liquid nitrogen, was placed at the end of the reaction tube. The gas stream and the vacuum were produced by an oil forepump.

In order to extract a greater number of hydrogen atoms into the reaction vessel, the walls of the nozzle were covered with phosphoric acid. We began with the idea that the formation of HO_2 (by the interaction of H and O_2) is a trimolecular reaction. Because Hudson and Foner [8] did not observe HO_2 at low pressures, but did observe HO_2 mass spectrometrically (by the reaction of $H + O_2$) at pressures of about 20 mm, the present experiments were carried out at a pressure of 60 mm. The principal pressure in the reaction vessel was created by the hydrogen. The temperature was room temperature. The admission of molecular oxygen to the reaction vessel led to the formation of hydrogen peroxide which, after freezing, was observed in the trap cooled with liquid nitrogen. The quantity of peroxide was determined by titration with a solution of potassium permanganate (0.05 N) in an acidic medium. The minimum

determinable quantity of peroxide by this method is $3 \cdot 10^{-7}$ moles. About $(6-7) \cdot 10^{-6}$ moles of H_2O_2 was ordinarily observed after the reaction.

Preliminary experiments (without the addition of O_2) were carried out for various pressures of hydrogen in the discharge. These experiments showed that hydrogen peroxide was not formed in the absence of O_2; however, the formation of water was observed, this being dependent on a small impurity of oxygen in the hydrogen. It was important to prove that the formation of hydrogen peroxide under these conditions was associated with the radical HO_2 because we had observed hydrogen peroxide during earlier investigations in which a discharge tube was used at pressures of about 6 mm for the reaction $H + O_2$ [9]. However, another mechanism for the formation of hydrogen peroxide – not involving HO_2 – occurs when the reaction is carried out at a low pressure [9] and at a temperature of approximately 100°. It was found [9] that the principal reaction between H and O_2 was the reaction occurring on the surface with the formation of OH and O, and not with the formation of HO_2. The formation of the hydrogen peroxide then occurred on the cold walls of the trap cooled in liquid nitrogen. So, if the formation of peroxide in the present experiments was associated with a surface reaction, a decrease of the pressure should favor the formation of H_2O_2, since the diffusion of hydrogen atoms to the wall would be facilitated.

Length of reaction vessel, cm	Quantity of peroxide in 20 min, $M \cdot 10^{-6}$
40	5.0
120	4.8
440	5.1

Experiments were carried out at a low pressure, and experiments were also run relating the dependence of the peroxide yield to the length of the reaction vessel. Experiments carried out at a pressure of 10 mm under conditions otherwise the same as those of experiments at 60 mm, yielded practically no hydrogen peroxide. The participation of a third particle (molecule of H_2) in the mechanism for the formation of H_2O_2 was definitely shown by the decrease of the formation of hydrogen peroxide when the pressure was lowered. The experiments relating the dependence of the rate of formation of peroxide to the length of the reaction vessel are cited in the table.

Fig. 2. The EPR spectrum of the HO_2 radical at the temperature of liquid nitrogen in the solid state as frozen from the gaseous state.

The table shows that there is no dependence of the rate of formation of H_2O_2 on the distance of the cold walls of the trap from the place where H mixes with O_2. This means that the formation of H_2O_2 is not associated with the cold walls, but occurs in the gas space. From these experiments one can draw conclusions about the mechanism of the HO_2 reaction under these conditions. The influence of the third body indicates that the principal reaction is the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$.

Since the formation of H_2O_2 is completed within a distance of 40 cm from the point of mixing of H with O_2 at a stream velocity of 90 cm/sec, it may be concluded that the HO_2 radical rather rapidly is transformed into H_2O_2 by the reaction $2HO_2 \rightarrow H_2O_2 + O_2$.

The formation of H_2O_2 by the reaction $HO_2 + H_2 \rightarrow H_2O_2 + H$ is excluded by the low temperature. We attempted to condense the HO_2 radical in a trap cooled with liquid nitrogen, and placed at a distance of 4 cm from the mixing point of H with O_2. This experiment was successful. A photograph of the EPR spectrum of the frozen condensate is shown in Fig. 2.* As is apparent from Fig. 2, the signal has an unsymmetrical form; the g factor is close to the g factor of diphenylpicrylhydrazyl. The total width of the signal was 23-26 oersteds. The signal disappeared when the condensate melted. An attempt to freeze out HO_2 at a distance of 1 meter from the point of mixing of H with O_2 was unsuccessful, in agreement with the data of the table, which indicates that the HO_2 is already converted to H_2O_2 at a distance of 40 cm. The spectrum of the condensate frozen during an experiment carried out without the addition of O_2 (a blank experiment) was made. Practically no signal was obtained in this case. There is thus no doubt of the correctness of the suggested mechanism for the interaction of H with O_2 according to the equation $H + O_2 + H_2 \rightarrow HO_2 + H_2$.

The rate constant for the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$ was measured by the method suggested earlier [7].

*The EPR spectrum of the HO_2 radical was taken by G. A. Kapralova with an IKhF-2 spectrometer.

For the determination of the rate constant of the reaction $H + O_2 + H_2$ it was necessary to measure the rate of accumulation of the primary product, and its dependence on the rate of addition of molecular oxygen. The primary product of this reaction is the HO_2 radical, whose concentration we were not able to measure directly. However, under the conditions of our experiment, the HO_2 radical is transformed into peroxide through the interaction of two HO_2 radicals.

The dependence of the final concentration of the primary product $(H_2O_2)_K$ on the initial concentration of oxygen $(O_2)_0$, was determined on the basis of the following scheme:

$$H + O_2 + H_2 \xrightarrow{k} HO_2 + H_2 \quad (1)$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (2)$$

$$H + H + H_2 \xrightarrow{k'''_H} 2H_2, \quad (3)$$

where k'''_H is the rate constant for the disappearance of the hydrogen atoms.

From the conditions of the stoichiometry, the final concentration of hydrogen peroxide $(H_2O_2)_K$, which was experimentally measured, could be expressed in the following way:

$$(H_2O_2)_K = (O_2)_0 - (O_2)_K, \quad (4)$$

where $(O_2)_K$ is the final concentration of molecular oxygen.

Let us write the following equation on the basis of the mechanism:

$$\frac{d(H)}{dt} = -k(H)(O_2)(H_2) - k'''_H (H)^2 (H_2) \quad (5)$$

$$\frac{d(O_2)}{dt} = -k(H)(O_2)(H_2). \quad (6)$$

Dividing (5) by (6) we obtained:

$$\frac{d(H)}{d(O_2)} = 1 + \frac{k'''_H (H)}{k(O_2)}. \quad (7)$$

The solution of the differential equation (7) leads to the following dependence of (H) on (O_2):

$$(H) = \frac{k}{k - k'''_H}(O_2) + C(O_2)^{\frac{k'''_H}{k}}, \quad (8)$$

where C is the integration constant which is determined from the boundary conditions: when $(H) = (H)_0$; $(O_2) = (O_2)_0$, where $(H)_0$ is the initial concentration of the hydrogen atoms.

Under the conditions of our experiment, the concentrations (H_2O_2) and (O_2) will cease to change, that is, will become the final concentrations when all of the atoms of hydrogen have been used up. The justification for this condition: $(H_2O_2) = (H_2O_2)_K$ and $(O_2) = (O_2)_K$, when $(H) = 0$, is clear from the table, since the quantity of peroxide remains constant when the reaction zone is lengthened.

Using the condition: $(O_2) = (O_2)_K$, when $(H) = 0$, and changing $(O_2)K$ to $(O_2)_0 - (H_2O_2)_K$, we obtain from Eq.(8):

$$-\frac{k}{k - k'''_H}[(O_2)_0 - (H_2O_2)_K] + \left[(H)_0 - \frac{k}{k - k'''_H}(O_2)_0\right]\left[1 - \frac{(H_2O_2)_K}{(O_2)_0}\right]^{\frac{k'''_H}{k}} = 0.$$

Since $\frac{(H_2O_2)_K}{(O_2)_0} \ll 1$, the quantity $\left[1 - \frac{(H_2O_2)_K}{(O_2)_0}\right]^{\frac{k'''_H}{k}}$ can be expanded as a series.

Limiting ourselves to the first two members of the series, we obtain the equation

$$\frac{1}{(H_2O_2)_K} = \frac{1}{(H)_0} + \frac{k'''_H}{k(O_2)_0}. \quad (9)$$

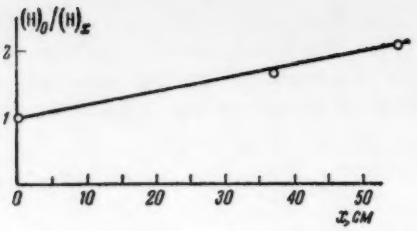

Fig. 3. The dependence of the relative concentration of hydrogen atoms $(H)_0/(H)_x$ on the distance x.

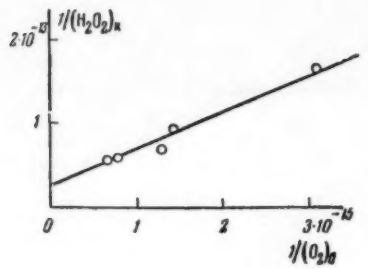

Fig. 4. The dependence of the reciprocal value of the final concentration of hydrogen peroxide $1/(H_2O_2)_K$ on the reciprocal value of the initial concentration of oxygen molecules $1/(O_2)_0$.

The equation (9) is the equation of a straight line in the coordinates $1/(H_2O_2)_K$, $1/(O_2)_0$. The constant k can be directly determined from the tangent of the angle of inclination according to the equation

$$k = \frac{k_H'''}{\operatorname{tg}\alpha}. \qquad (10)$$

In order to determine k, it is necessary to measure the dependence of $(H_2O_2)_K$ on $(O_2)_0$, and also to know the rate constant for the disappearance of the hydrogen atoms, and that it has been found that this disappearance follows the termolecular law $H + H + H_2 \rightarrow H_2 + H_2$, i.e., is quadratic. We could have made use of the data of other authors on the rate constant for the recombination of hydrogen atoms. However, it was important for us to measure the rate constant for the disappearance of hydrogen atoms under the conditions of our experiments. For the measurement of the rate constant for the disappearance of hydrogen atoms, we used the method for the measurement of rate constants of the disappearance of atoms and radicals which we had published earlier [10]. Based on this method, the change in the concentration of hydrogen atoms as a function of the length of the reaction vessel for the case of a predominantly quadratic disappearance may be written in the form

$$\frac{(H)_0}{(H)_x} = 1 + \frac{xk_H'''(H)_0(H_2)}{w}, \qquad (11)$$

and for the case of a predominantly linear disappearance,

$$\lg\frac{(H)_0}{(H)_x} = \frac{k_H x}{w}0{,}43, \qquad (12)$$

where $(H)_x$ is the concentration of H atoms at the distance x; k_H is the rate constant for the linear disappearance of H; w is the linear stream velocity.

By measuring the dependence of $(H)_0/(H)_x$ on x, and constructing the graph, one can determine whether it is the quadratic recombination of the H atoms which predominates.

If the points on the graph of the dependence of $(H)_0/(H)_x$ on x fall on a straight line which intercepts the ordinate axis at unity, then the quadratic recombination is predominant. Figure 3 shows the straight line obtained from the experimental points for experiments done at room temperature with p_{H_2} = 60 mm and w = 90 cm/sec. The concentration of hydrogen atoms in various positions in the reaction vessel along the stream path was measured by the maximum yield of hydrogen peroxide for the introduction of molecular oxygen into those positions of the reaction vessel.

The experimental points taken over a large range of values of x (55 cm) fall closely on a straight line intercepting the ordinate axis at unity. However, a straight line which begins at the origin is also obtained for the coordinates $\log[(H)_0/(H)_x]$, x. In order to choose which law is obeyed during the disappearance of the hydrogen atoms, it is necessary to turn to a theoretical examination of the various cases of the ratios of the linear and quadratic disappearance constants which were determined earlier [10]. In one case, when the linear disappearance was small in absolute value and the quadratic disappearance exceeded the linear by three or four times, a straight line was obtained in the coordinates $(H)_0/(H)_x$, x and a curve (nearly a straight line) was obtained in the coordinates $\log[(H)_0/(H)_x]$, x. Our experimental data approach this situation. Consequently, the predominating disappearance is a quadratic one and, therefore, the value $k_H'''(H)_0$ is determined from the graph of Fig. 3, according to the equation

$$k_H'''(H)_0 = \frac{w\operatorname{tg}\beta}{(H_2)}. \qquad (13)$$

The following value of this quantity was obtained:

$$k_H'''(H)_0 = 9 \cdot 10^{-19}\ \text{cm}^3 \cdot \text{sec}^{-1} \cdot \text{molecules}^{-1}.$$

The value used for the initial concentration of hydrogen atoms $(H)_0$ was $1.72 \cdot 10^{13}$ molecules/cm^3 in measuring the dependence of $(H)_0/(H)_x$ on x. It follows from this that $k_H''' = 5.2 \cdot 10^{-32}$ $cm^6 \cdot sec^{-1} \cdot molecules^{-2}$.

This value of k_H''' is in good agreement with the values of other authors: Farkas and Sachsse [1], $k_H''' = 9.3 \cdot 10^{-32}$; Smallwood [4], $4.65 \cdot 10^{-32}$; Steiner [5], $3.5 \cdot 10^{-32}$; Amdur [6], $3.3 \cdot 10^{-32}$ (in $cm^6 \cdot sec^{-1} \cdot molecules^{-2}$).

We measured the dependence of $(H_2O_2)_K$ on $(O_2)_0$ for the determination of the rate constant of the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$. The experimental data collected at room temperature for $p_{H_2} = 60$ mm and w = 90 m/sec are given in Fig. 4. From the tangent of the angle of inclination of the straight line (Fig. 4), and the value k_H''' = $= 5.2 \cdot 10^{-32}$, the value of the termolecular rate constant for the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$ according to Eq. (10) is

$$k = 1.2 \cdot 10^{-33} \text{ cm}^6 \cdot \text{sec}^{-1} \cdot \text{molecules}^{-2}.$$

This rate constant agrees with the data of Nalbandyan and Voevodskii [3] ($2.4 \cdot 10^{-33}$); it is by one order of magnitude larger than the data of Farkas and Sachsse [1], and is by one order of magnitude smaller than the data of Cook and Bates [2].

In conclusion, the authors express their gratitude to G. A. Kapralova for the determination of the EPR spectrum of the HO_2 radical.

SUMMARY

1. The rate constant of the termolecular process for the formation of HO_2 by the reaction of hydrogen atoms with molecular oxygen at room temperature was measured.

2. The rate constant for the recombination of hydrogen atoms in triple collisions was measured.

3. The EPR spectrum of the HO_2 radical was determined at the temperature of liquid nitrogen as frozen from the gas phase.

4. The great activity of the HO_2 radical toward conversion to H_2O_2 was observed.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

STUDY OF THE VIBRATION SPECTRA OF METHACRYLIC ACID DERIVATIVES CONTAINING GROUP IV ELEMENTS

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There have recently appeared in the literature communications concerning the synthesis and study of the polymerization properties of methacrylic and acrylic acid derivatives containing group IV elements, for example, trialkyl- and aryltin methacrylates and acrylates [1-4] and trialkylgermanium methacrylates [5].

The present communication is devoted to a study of the vibration spectra of silicon, germanium, and tin methacryl derivatives. The methods used to prepare the cited compounds are given in the experimental part, and their properties are summarized in the table. We obtained the Raman spectra of triethylsilanol methacrylate, triethylgermanium methacrylate, triethyltin methacrylate, and, for comparison, methyl methacrylate.* The Raman spectra were photographed in an ISP-51 spectrograph with a central cell, using the 4358 A mercury line for excitation. The intensities were classified in a visual scale numbered from one to ten. The solid triethyltin methacrylate was studied in benzene; therefore, its Raman spectrum is imperfect, since it is necessary to assume the presence of Raman lines in those regions where the much more intense absorption lines of benzene are situated (in the regions 900-1000, 1580 to 1620, and 2950-3100 cm^{-1}). Infrared (IR) spectra of triethylsilanol methacrylate, triethylgermanium methacrylate, triethyltin methacrylate, and also tripropyltin methacrylate were obtained in the 700-1800 cm^{-1} region with a UR-10 spectrograph.

Unadulterated liquid silicon and germanium methacrylates (thickness of the absorbing layer was 0.02 mm) and solid tin methacrylates compressed with powdered potassium bromide were used. In addition, the IR spectrum of a 2% triethyltin methacrylate solution in benzene was obtained in the 1500-1800 cm^{-1} region for comparison with the Raman spectrum. The spectra are shown in Table 1 and Fig. 1. The IR spectrum of methyl methacrylate, obtained by Chumaevskii and reported earlier [5], is also shown. The great similarity between the IR and Raman spectra of the silicon and germanium methacrylates, which would be expected from the similarity of the chemical and physical properties of these elements, can be seen by inspection of Table 1 and Fig. 1. The ascribing of the frequencies in these spectra is not particularly difficult. It is known [7-10] that the group of atoms $-C\lessgtr^{O}_{O}$ in unsaturated esters is characterized by absorption in the 1715-1730 cm^{-1} region [stretching vibration of the $>C=O$ bond ($\nu_{C=O}$) – intense both in the IR and in the Raman spectrum], and in the 1250-1320 and 1140-1205 cm^{-1} regions (very intense bands in the IR spectrum). In the methyl methacrylate spectra, the 1730 cm^{-1} band (in the IR and Raman spectra), and the two intense double IR bands, 1170-1200 and 1310-1330 cm^{-1}, evidently conform to this. With substitution of methyl groups in the triethylsilanol and triethylgermanium groups, the vibration frequency of the $>C=O$ bond decreases to 1695 and 1680 cm^{-1}, respectively. The bands associated with absorption by the $-C-O-$ group in the IR spectrum of triethylsilanol methacrylate are probably those with frequencies 1187-1205 and 1305-1330 cm^{-1} and 1190 and 1318-1338 cm^{-1} in the triethylgermanium methacrylate IR spectrum.

The $>C=CH_2$ group of atoms is characterized in the methyl methacrylate spectrum by the frequency 1645 cm^{-1} [stretching vibration of the C = C bond ($\nu_{C=C}$)] and by lines in the 3000-3100 cm^{-1} region (stretching vibration of the $=C-H$ bond). The same frequencies are observed in the silicon** and germanium methacrylate spectra.

*The methyl methacrylate Raman spectrum was reported earlier by Batuev et al. [6]. The spectrum photographed by us agreed, on the whole, with that reported.

**A weak line at frequency 1667 cm^{-1}, which is possibly explained by a small impurity of methacrylic acid formed through hydrolysis of triethylsilanol methacrylate (cf. [11]), is also observed in the Raman spectrum of the latter compound.

Raman and IR Spectra of Group IV Element Methacryl Derivatives

$CH_2=C(CH_3)COOCH_3$	$CH_2=C(CH_3)COOSi(C_2H_5)_3$		$CH_2=C(CH_3)COOGe(C_2H_5)_3$			$CH_2=C(CH_3)COOSn(C_2H_5)_3$	
Raman	IR	Raman	IR	Raman	Raman polymer	IR	Raman in benzene
170 (2)		169 (1)		160 (2br)			
226 (2)				219 (2br)			
				243 (1)	237 (i)		
		298 (br)		292 (2br)	293 (1br)		
				331 (1br)	325 (1br)		
		368 (1)		360 (1br)			
381 (7br)		396 (3do)		380 (1)			
453 (1)							
512 (4)							490 (10)
		573 (7)		550 (10br)	547 (10br)		522 (5)
		587 (6)					
	690 (av)						
	740 (v.i.)		710 (av)	594 (7br)	592 (6br)		577 (2)
		745 (1br)		671 (i,br)			641 (i)
603 (5)	795 (w)	800 (6)				683 (av)	
	822 (i)						
			825 (i)				797 (1)
			849 (av)	794 (2)			
	850 (w)		936 (i)	831 (i)	823 (3)	827 (av)	
	947 (i)			849 (7sh)		853 (av)	
836 (9sh,do)		952 (3br)	974 (w)	945 (2)		930 (av)	
	970 (w)	979 (2br)				957 (av)	
943 (2br)	1010 (v.i.)		1012 (i)	978 (4br)		973 (av)	
957 (1)		1015 (3br)			976 (4br)		
1005 (2)	1077 (av)			1014 (2br)			
		1111 (1br)		1030 (3br)	1018 (2br)	1011 (av)	1035 (1)
1030 (3br)		1140 (2br)		1111 (2br)	1105 (1br)	1098 (w)	
		1175 (1br)					1097 (i)
1108 (2br)							
	1187 (av)						
1166 (2br)	1205 (v.i.)		1190 (i, br)			1193 (av)	
	1225 (i)		1225 (av)		1227 (3br)	1230 (i)	1190 (3br)
1195 (2br)	1246 (w)	1238 (2br)		1230 (7br)			
	1305 (i)	1304 (1br)	1318 (av)				1245 (i)

(continued)

TABLE 1 (continued)

$CH_2=C(CH_3)COOCH_3$	$CH_2=C(CH_3)COOSi(C_2H_5)_3$		$CH_2=C(CH_3)COOGe(C_2H_5)_3$			$CH_2=C(CH_3)COOSn(C_2H_5)_3$	
Raman	IR	Raman	IR	Raman	Raman polymer	IR	Raman in benzene
	1330 (i)	1323 (1br)	1338 (i)	1345 (2br)			1286 (1)
1330 (1)	1435 (i)						
		1407 (8br)	1408 (w)	1402 (4)		1405 (av)	
1408 (8)	1462 (i)		1427 (w)	1430 (10,br)	1424 (1br)		
		1464 (7br)	1452 (i)	1463 (6br)	1462 (6br)	1456 (av)	
						1580 (w.i.)	1450 (i)
1450 (3br)	1635 (av)	1644 (8)	1638 (i)	1645 (8br)	1640 (v.i.)	1642 (av)	
		[1667 (1)]					1660 (2)
1642 (10)	1696 (i)	1695 (3br)	1677 (v.i.)	1685 (7sh)	1687 (1)		
1727 (9)		2882 (10)		2879 (8sh)	2877 (8)		
		2913 (4sh)		2912 (7)	2910 (7)		
		2938 (4)		2933 (8)	2934 (7)		2875 (3)
2937 (7)		2963 (6sh)		2963 (7)	2962 (7)		2917 (2)
2963 (7)		3000 (2)		2998 (2sh)	2999 (i)		
3005 (6)							
3029 (i)		3107 (4br)		3103 (2sh)			3005 (2)
3107 (4)							

Key: i - intense; v.i. - very intense; av - average; w - weak; sh - sharp; br - broad; do - double.

We note that in the IR spectra of C, Si, and Ge methacrylates, $\nu_{C=O}$ is more intense than $\nu_{C=C}$, and vice versa in the Raman spectra. The $(C_2H_5)_3Si$ group is characterized by the frequencies 573 and 587 cm^{-1} (symmetrical and unsymmetrical stretching frequencies of the Si–C bonds [12]) and 975, 1012, 1240, and 1463 cm^{-1} (stretching vibrations of the C–C bonds and deformation vibrations of the C–H bonds in the ethyl groups attached to the silicon [13]). Similarly, the $(C_2H_5)_3Ge$ group is characterized by frequencies 550 and 594 cm^{-1} (ν_{Ge-C}), and 977, 1015, 1230, and 1460 cm^{-1} [14].

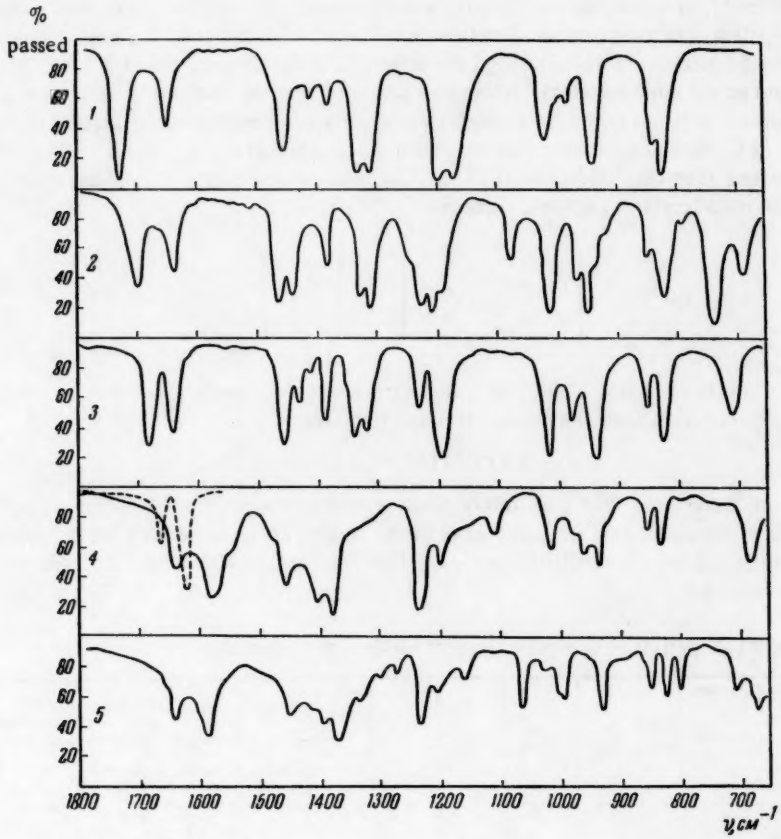
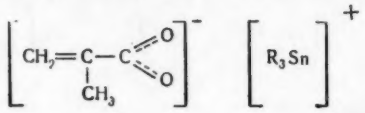


Fig. 1. IR spectra of $CH_2 = C(CH_3)COOMR_3$: 1) $CH_2 = C(CH_3)COOCH_3$; 2) $CH_2 =$ $= C(CH_3)COOSi(C_2H_5)_3$, 0.02 mm layer; 3) $CH_2 = C(CH_3)COOGe(C_2H_5)_3$, 0.02 mm layer; 4) $CH_2 = C(CH_3)COOSn(C_2H_5)_3$, 10 mg compressed with 2 g KBr. Dotted line – 2% solution in benzene. 5) $CH_2 = C(CH_3)COOSn(n\text{-}C_3H_7)_3$, 20 mg compressed with 2 g KBr.

Several hours after the Raman spectrum of triethylgermanium methacrylate had been obtained, this material polymerized into a very hard, transparent glass; this phenomenon was not observed with triethylsilanol methacrylate. The IR spectrum of triethylgermanium methacrylate is also shown in Table 1. It can be seen, from a comparison of the IR spectra of the monomer and polymer, that the lines corresponding to the stretching vibrations of the Ge–C bonds and characterizing the absorption by the ethyl groups attached to the germanium, as would be expected, did not change either in frequency or intensity. At the same time, the lines corresponding to the presence of the C=C bond in the molecule (1645, 2998, and 3103 cm^{-1}) have disappeared, or almost disappeared, from the polymer spectrum. The very sharp, intense 849 cm^{-1} line, which on these grounds must evidently correspond to nonplanar vibrations of the $C=C\diagup^{H}$ bond, has also disappeared. It is interesting to note that the intensity of the line corresponding to the vibration of the C=O bond falls sharply in the polymer spectrum. It is possible that this depends on the interaction between carbonyl groups of one polymer chain and germanium atoms of another, as was proposed [5] in

order to explain the increase in softening point of polytriethylgermanium methacrylate in comparison with polymethyl methacrylate.

The frequencies are less accurately ascribed in the case of tin methacrylates because the vibration spectra of organotin compounds have been little studied as yet. The intense lines at frequencies 490 and 529 cm^{-1} in the Raman spectrum of triethyltin methacrylate dissolved in benzene undoubtedly correspond to the stretching vibrations of the Sn–C bonds [15]. In the IR spectra of tin methacrylates (material compressed with potassium bromide) there are two bands, 1642 and 1580 cm^{-1}, of which the second is the more intense, in the region of the double-bond frequencies. In the IR spectrum of triethyltin methacrylate dissolved in benzene, the 1657 and 1615 cm^{-1} bands correspond to those given above (the frequencies increase through the influence of the solvent; the 1660 cm^{-1} line is also observed in the Raman spectrum of the same solution). It can be considered that the 1642 cm^{-1} band (and, correspondingly, the 1660 cm^{-1} in benzene solution) in the tin methacrylate spectra correspond to the vibration of the C=C bond, just as in the spectra of C, Si, and Ge methacrylates. Then the absence of $\nu_{C=O}$ in the region 1670-1700 cm^{-1}, and the presence of strong 1580 cm^{-1} IR bands (1615 cm^{-1} in benzene solution) in tin methacrylate spectra leads to the conclusion that tin methacrylates are ionic compounds of the type



with equalized C–O bonds in the anion. This conclusion agrees with the conclusions drawn by Okawara et al. [16], from studies of the IR spectra of silicon and tin acetates and formates.

EXPERIMENTAL

Triethylsilanol methacrylate. 26.4 g of freshly distilled triethylsilanol [b.p. 57-59° (6 mm; $n^{20}D$ 1.4300] and 17.2 g freshly distilled methacrylic acid were heated in 30 ml boiling dry acetone for 2 hr; the solvent was then distilled off, after which the residue was distilled under vacuum. The yield of triethylsilanol methacrylate was 26.4 g, this being 66% of theoretical.

TABLE 2. Properties of Group IV Element Methacryl Derivatives

$CH_2=C(CH_3)-COOMR_3$		B.p., °C (mm Hg)	n_D^{20}	d_{20}^{20}	Yield, %	MR		Analysis, %		Literature references
M	R					calc.	found	calc.	found	
Si	C_2H_5	60,5(6)	1,4393	0,9058	66	58,35	58,20	C 59,70 H 10,02 Si 14,36	59,42 10,22 14,72	[17]
Ge	C_2H_5	69—70(5)	1,4569	1,1439	61	58,55	58,28	C 49,05 H 8,23 Ge 29,65	48,60 8,17 29,83	[5]
Sn	C_2H_5	m.p. 74—75°	—	—	69	—	—	—		[4]
Sn	C_3H_7	48,5—49	—	—	83	—	—			[4]

Triethylgermanium methacrylate.* 5 g of dehydrated potassium methacrylate, 60 ml absolute methanol, and a small amount of cuprous chloride were placed in a three-necked flask fitted with a reflux condenser, stirrer, and a dropping funnel. 10 g triethylgermanium bromide was slowly added to the mixture which was heated for 1 hr, then left overnight. Precipitated potassium bromide was filtered off, the filtrate was concentrated under a vacuum of 15 mm (produced with a water-jet pump), at a temperature not exceeding 50°, then the residue was distilled under vacuum. The yield of triethylgermanium methacrylate was 6 g, this being 61% of theoretical.

*Synthesized by N. V. Klimentov

Triethyl- and tripropyltin methacrylates. 2.9 g triethyltin hydroxide, m.p. 43°, prepared by alkaline hydrolysis of triethyltin bromide [b.p. 85-86 (8 mm); $n^{20}D$ 1.5320], was mixed with 2 ml water and 0.9 ml freshly distilled methacrylic acid; the white crystalline deposit which formed was washed with water, in order to remove residual raw materials, and dried in a vacuum desiccator. The yield of triethyltin methacrylate was 1.9 g, this being 69% of theoretical. Tri-n-propyltin methacrylate was prepared in a similar manner. The properties of the prepared compounds are given in Table 2.

SUMMARY

1. Raman and IR spectra of silicon, germanium, and tin methacrylates were obtained.

2. The −O−M— (M−C, Si, or Ge) bond is covalent in carbon, silicon, and germanium methacrylates; tin methacrylates are ionic compounds.

3. Triethylgermanium methacrylate polymerizes, when exposed to radiation from a quartz mercury vapor lamp, by means of C=C bonds, possibly with simultaneous interchain reaction between carbonyl groups and metal atoms.

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THE REACTION OF ORGANIC MAGNESIUM COMPOUNDS WITH (FERROCENYLMETHYL)TRIALKYLAMMONIUM SALTS

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The replacement of the trialkylammonium group in (ferrocenylmethyl)trialkylammonium salts occurs under mild conditions with good yields. Such reactions occur more easily in the ferrocene series than in the benzene series, and are sufficiently diversified to use for the synthesis of ferrocene derivatives [1,2]. This gave us a reason to assume that the reaction of (ferrocenylmethyl)trialkylammonium salts with organic magnesium compounds would also occur more easily than with salts of the benzene series, and could be used for obtaining ferrocene derivatives.

In the present work, we have carried out the reaction of (ferrocenylmethyl)trialkylammonium salts with organic magnesium compounds, and have obtained, by this process (in yield of 30-60%) benzylferrocenyl methane, allylferrocenyl methane, α-naphthylferrocenyl methane, propyl-, allyl-, benzyl-, and ethylferrocenes (the first five compounds had not previously been described)

$$C_5H_5FeC_5H_4CH_2NR'_3X + RMgX \rightarrow C_5H_5FeC_5H_4CH_2R + NR'_3 + MgX_2$$

The reaction was carried out in ether, in mixtures of ether and tetrahydrofuran, or in dibutyl ether. As the ammonium salt we used N,N-dimethylaminomethylferrocene methiodide and bromoethylate.

The reaction of the organic magnesium compounds with (ferrocenylmethyl)trialkylammonium salts was apparently heterolytic. The stability of the ferrocenylmethyl cation $C_5H_5FeC_5H_4CH_2^+$ has been observed several times before [3,4] and is probably due to rupture of the C–N bond under the attack of the carbanion of the organic magnesium compound. On reaction of (ferrocenylmethyl)trimethylammonium iodide with allyl magnesium bromide, along with the ferrocenylallyl methane there was formed a small amount of symmetrical diferrocenylethane. The side products obtained as a result of doubling of the radical of the organic magnesium compound were isolated in the case of reaction with phenyl magnesium bromide and with benzyl magnesium chloride (respectively, diphenyl and dibenzyl). When these substituted ferrocenes were purified by chromatography on aluminum oxide, it was noted that there was a change in some part of the substance and a compound was formed with a brighter color, in which the ketone group was found spectroscopically. In the case of benzylferrocene, we also isolated benzoylferrocene and identified it by melting point and mixed melting point. Hence, on aluminum oxide in the presence of oxygen of the air there is oxidation of the methylene group connected with the ferrocene nucleus.

EXPERIMENTAL

To 0.02-0.13 M of organic magnesium compound we added 0.03 M of N,N-dimethylaminomethylferrocene methiodide or bromoethylate,* first dried over P_2O_5 for three days, then treated with 100 ml of absolute tetrahydrofuran (distilled over $LiAlH_4$) or 150 ml of absolute n-butyl ether, and the reaction mixture was heated in an atmosphere of pure nitrogen for 20 hr (in the case of benzyl magnesium bromide, the reaction mixture was heated for 10 hr) to boiling, if the reaction was carried out in diethyl ether or in its mixture with tetrahydrofuran. If the solvent was dibutyl ether, the reaction was carried out at 110-120° and the diethyl ether was first distilled off. The reaction took place in diethyl ether with C_6H_5MgBr, in the mixture of diethyl ether – tetrahydrofuran with $C_6H_5CH_2MgCl$,

*The ratios of (ferrocenylmethyl)trialkylammonium salt and organic magnesium compound are given in the table. The organic magnesium compound was obtained in a medium of diethyl ether from equimolecular amounts of magnesium and halogen derivative (except for allyl magnesium bromide, where the ratio was 2:1, respectively). The yield of organic magnesium compounds was considered to be quantitative.

R	Constants				Yield, %	Found, %			Calculated, %			RMgX used	Ratio, ammonium salt:RMgX
	m.p., °C	b.p., °C, press., mm Hg	d_4^{20}	n_D^{20}		C	H	Fe	C	H	Fe		
C_6H_5[1]	74,5—75,5	—	—	—	27	74,08 73,9	6,02 6,00	19,84 19,89	73,93	5,85	20,22	C_6H_5MgBr[2]	1 : 2,5
$CH_2C_6H_5$[3]	57—58	—	—	—	60	74,45 74,60	6,41 6,50	19.0(19,11	74,49	6,26	19,24	$C_6H_5CH_2MgCl$[2]	1 : 12
$C_{10}H_7=\alpha$	114—115	—	—	—	51	77,25 77,13	5,66 5,68	17,22 17,12	77,31	5,56	17,12	$C_{10}H_7MgBr$[4]	1 : 2,5
$CH=CH_2$[5]	—	93—95 (1)	1,2082	1,5990	34	68,89 68,8	6,51 6,49	24,25 24,23	69,07	6,24	27,41	$CH_2=CHMgBr$	1 : 5
$CH_2CH=CH_2$	—	128—130 (1)	1,2022	1,5940	53	70,35 70,3(	6,89 6,82	23,04 23,05	70,13	6,7	23,26	$CH_2=CHCH_2MgBr$	1 : 20
CH_3[6]	—	93—94 (1)	—	1,6002	59	67,19 67,30	6,63 6,68	25,98 25,88	67,35	6,59	26,10	CH_3MgI[4]	1 : 3,7
CH_2CH_3	—	106—108 (3)	1,2102	1,5880	63	68,46 68,32	7,30 7,21	24,25 24,48	68,50	7,06	24,44	CH_2CH_2MgBr[2]	1 : 6

[1]Literature data for benzylferrocene [5,7]: m.p. 76°, b.p. 73-74°. Mixed sample with benzylferrocene obtained by reduction of benzoylferrocene [5,6] melted without depression. From the reaction product we isolated 0.2 g of diphenyl (on chromatography on Al_2O_3 it washed out before the benzylferrocene); m.p. 68.5-70° (from alcohol). The literature gives for diphenyl [8,9] m.p. 70.5°.

[2]The reaction was carried out with (ferrocenylmethyl)trimethylammonium iodide.

[3]We isolated from the reaction product 0.3 g of dibenzyl, m.p. 49-51° (on chromatography on Al_2O_3 we washed it out before the benzylferrocenylmethane). The literature gives for dibenzyl [10] m.p. 52°.

[4]The reaction was carried out with (ferrocenylmethyl)dimethylethylammonium bromide.

[5]We isolated from the reaction product 1,2-diferrocenylethane (on chromatography on Al_2O_3 we washed it out after allylferrocene with a mixture of 1:1 ligroin with benzene); m.p. 193-195° (from a mixture of ligroin with benzene). A mixed m.p. with known 1,2-diferrocenylethane gave no depression. The literature gives for 1,2-diferrocenylethane [4,11] m.p. 193-195°; m.p. 200-200.5°.

[6]The literature gives for ethylferrocene [12] b.p. 108-109° (5.5 mm; $n^{20}D$ 1.6017).

CH_2 = $CHCH_2MgBr$, and CH_2 = $CHMgBr$, and in dibutyl ether with CH_3MgI, C_2H_5MgBr, and α-$C_{10}H_7MgBr$. It should be noted that the solvent strongly affects the yield of alkylation products. Thus, in preparing benzylferrocene, by replacement of diethyl ether by its mixture with tetrahydrofuran or in dibutyl ether the yield fell from 27 to 9 and 4%, respectively.

The reaction mixture was decomposed with dilute hydrochloric acid. The water layer was extracted with ether. The ether extracts were added to the ether – tetrahydrofuran solution (or the solution in dibutyl ether) and the mixture was washed with water, with soda solution, and again with water, and dried over sodium sulfate. The solvent was distilled (the dibutyl ether was distilled in a vacuum under nitrogen); the residue was dissolved in ligroin and chromatographed on Al_2O_3. The resulting ferrocene derivative was washed out with ligroin. Then the solid substances were recrystallized from ligroin or hexane, and the liquids were distilled in a vacuum under nitrogen; the constants and yield are given in the table.

On chromatography of these compounds on Al_2O_3 there was a change in some of the compounds and formation of a substance with a brighter color which remained on the column during washing out with ligroin, and was washed out with ether. On repeated chromatography, the substance washed from the column with ligroin again formed the compound with the brighter color. In the infrared spectrum of this compound there were frequencies which were characteristic of the carbonyl group. The benzoylferrocene which formed in the chromatography of benzylferrocene was isolated and identified. After two chromatographic separations of 0.8 g of benzylferrocene we obtained 0.2 g of benzoylferrocene which was purified by chromatography on Al_2O_3 (eluting with a mixture of 1:1 benzene and ether), and was recrystallized from ligroin; its m.p. and the m.p. of a mixed sample with known substance was 106-107°. The literature [5,6] gives, for benzoylferrocene, m.p. 108-109°.

SUMMARY

1. We have obtained benzylferrocenyl methane, allylferrocenyl methane, α-naphthylferrocenylmethane, propyl-, allyl-, benzyl-, and ethylferrocene by reaction of organic magnesium compounds with (ferrocenylmethyl)-trialkylammonium salts.

2. Benzylferrocene is oxidized to benzoylferrocene on chromatography on aluminum oxide.

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THE SYNTHESIS OF α-CHLORO-ω-SULFOCARBOXYLIC ACIDS

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The great availability of α,α,α,ω-tetrachloroalkanes, obtained by telomerization of ethylene with carbon tetrachloride, and their property of reacting with nucleophilic, electrophilic, and radical reagents, permits a wide system of syntheses of bifunctional compounds based on them [1]. In the present paper, we describe methods for preparing α-chloro-ω-sulfocarboxylic acids. Compounds of this type have been studied very little. α-Chloro-ω-sulfocarboxylic acids are of interest as starting substances for the synthesis of various polyfunctional compounds, especially α-amino-ω-sulfocarboxylic acids. Two of us, with Kost and Vasil'eva [2-5], worked out a method of synthesis for α-chlorocarboxylic acids by coupled chlorination, of compounds which contained $CCl_2=CH$ groups, in a medium of sulfuric, formic, or acetic acids; in the latter case it was necessary to add equimolecular amounts of mercuric acetate. For the case of sulfuric acid, the reaction took place by the scheme

$$X(CH_2)_nCH=CCl_2+Cl_2\xrightarrow{H_2SO_4}X(CH_2)_nCHClCCl_2OSO_3H\xrightarrow{H_2O}X(CH_2)_nCHClCOOH.$$

Based on this method, we studied two paths of synthesis for the α-chloro-ω-sulfocarboxylic acids: starting from sulfates with the structure $NaO_3S(CH_2)_nCH=CCl_2$ (I) and chlorides of isothiuronium derivatives with the structure $HCl\cdot NH_2(NH=)CS(CH_2)_nCH=CCl_2$ (II). Compounds (I) and (II) were obtained from α,α,α,ω-tetrachloroalkanes [6-8]. The chlorination of (I) was carried out in anhydrous formic acid, and here, usually, along with the "coupled chlorination," there also occurred addition of chlorine to the double bond:

$$NaO_3S(CH_2)_nCH=CCl_2+Cl_2\xrightarrow{HCOOH}\begin{cases}NaO_3S(CH_2)_nCHClCO_2H\\NaO_3S(CH_2)_nCHClCCl_3\end{cases}$$

Chlorination of (II) occurs in an analogous way:

$$CCl_2=CH-(CH_2)_nSC(=NH)NH_2\cdot HCl\xrightarrow[HCOOH]{Cl_2}\begin{cases}COOH-CHCl-(CH_2)_nSO_3H\\CCl_3CHCl(CH_2)_nSO_3H\end{cases}$$

In this reaction there is a combination of coupled chlorination of the dichlorovinyl group with transformation of the isothiuronium group into SO_3H. Also, in some experiments, we isolated from the reaction mixture a substance whose elementary analysis corresponded to the formula $Cl-C(=NH)NH_2\cdot HCl$. A compound of this composition was obtained in chlorination of S-alkylisothiuronium salts [9]. As is known, chlorination of S-alkylisothiuronium salts in a water solution was previously suggested as a method for the synthesis of alkylsulfonyl chlorides [9,10], but in several cases an explosion occurred in the isolation of the alkylsulfonyl chlorides from the reaction mass [11]. Under the conditions of our experiments, no explosion occurred.

The separation of the sulfoacids was easily carried out due to the markedly lower solubility in water of the tetrachloroalkylsulfoacids as compared to the α-chloro-ω-sulfocarboxylic acids. The first compounds were separated as their sodium salts, the second were identified in the form of their bis-S-benzylisothiuronium salts: $HO_2C-CHCl-(CH_2)_nSO_3H\cdot 2C_6H_5CH_2SC(=NH)NH_2$.

Variation in the rate of flow of chlorine from ≈15 to ≈50 ml/min and of reaction temperature from 20-50° did not affect the yield of the final product. However, with increase in rate of passing chlorine, the reaction occurred more quickly. Comparison of the yields of products in the synthesis by both schemes permitted the following preliminary conclusions. To obtain a high yield of α-chloro-ω-sulfocarboxylic acid it is best to use isothiuronium chloride derivatives with the general formula $CCl_2=CH-(CH_2)_nSC(=NH)NH_2\cdot HCl$, since, in this case, the

chlorosulfocarboxylic acid is obtained with a higher yield and in a more pure form. α-Chloro-β-sulfopropionic acid is an exception; it was obtained from sodium 3,3-dichloro-2-propenylsulfonate with a high yield.

EXPERIMENTAL

5,5-Dichloro-4-pentenyl isothiourea hydrochloride. A mixture of 5.19 g of 1,1,5-trichloro-1-pentene and 2.28 g of thiourea and a solution of a small amount of KI in 15 ml of acetone was heated on a boiling water bath in a sealed ampule for 27 hr. After distillation of the acetone, a crystalline hydrochloride precipitated from the residue, 4.3 g or 57.3% of the theory. After three recrystallizations from acetone, the hydrochloride of 5,5-dichloro-4-pentenyl isothiourea melted at 98-99°. Found: C 28.85, 28.83; H 4.16, 4.19%. $C_6H_{11}Cl_3N_2S$. Calculated: C 28.85; H 4.40%. Later, this reaction was carried out without addition of KI while heating for 36 hr. The yield was 60% of the theory.

In an analogous way we obtained chlorides of isothiuronium derivatives of other α,α,ω-trichloroalkenes. For the "coupled chlorination" we used recrystallized samples. The isothiuronium salts were also obtained by heating in a flask under reflux an alcohol solution of thiourea and α,α,ω-trichloroalkene for 16 hr. This process [8] was suitable for obtaining large amounts of isothiuronium salts. The yield in this case was 55% of the theory.

Chlorination of $CCl_2=CH-CH_2-SO_3Na$. Through a solution of 5 g of sodium 3,3-dichloro-2-propenyl sulfonate in 25 ml of anhydrous formic acid was passed a stream of chlorine until absorption of chlorine by the reaction mixture stopped. There was slow warming to 30°. The reaction was diluted with warm water, upon which there was heating and evolution of HCl; then the water and formic acid were distilled off in a vacuum at 35-45°. A white precipitate of the monosodium salt of α-chloro-ω-sulfopropionic acid ($COOH-CHCl-CH_2-SO_3Na$) remained. Yield 4.4 g (81.6% of the theory). The product was recrystallized from water. Found: C 17.01, 16.95; H 1.96, 1.90; Cl 17.04, 16.85%. $C_3H_4O_5ClSNa$. Calculated: C 17.10; H 1.90; Cl 16.86%. Bis-S-benzylisothiuronium salt $[COOH-CHCl-CH_2SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2]$ had m.p. 154-155° (from water). Found: C 43.60, 43.55; H 4.78, 4.90; Cl 7.04, 7.29%. $C_{19}H_{25}O_5ClS_3N_4$. Calculated: C 43.84; H 4.80; Cl 6.82%.

Chlorination of $CCl_2=CH-(CH_2)_3SO_3Na$. The experiment was carried out like the preceding one. From 12 g of sodium 5 5-dichloro-4-pentenylsulfonate after distillation of the formic acid and water we obtained a mixture of crystalline sodium tetrachloroalkylsulfonate and α-chloro-ω-sulfoacid in the form of a very viscous oil. The crystals were separated by recrystallization of the mixture from water; weight 2.65 g. The filtrate was further evaporated in a vacuum and gave a further 1.55 g of crystals. The total yield of sodium 5,5,4,4-tetrachloroamylsulfonate was 4.2 g (27% of the theory). The product was recrystallized from water. Found: C 18.02, 18.21; H 2.66, 2.53%. $C_7H_{11}O_3Cl_4SNa \cdot H_2O$. Calculated: C 18.18; H 2.72%. S-Benzylisothiouronium salt $[CCl_3-CHCl-(CH_2)_3SO_3H \cdot C_6H_5CH_2SC(=NH)NH_2]$ had m.p. 150-151° (after three recrystallizations from water). Found: C 34.93; H 4.25%. $C_{13}H_{18}O_3Cl_4N_2S_2$. Calculated: C 34.22; H 3.97%.

We obtained 3.7 g of an oily product. By careful vacuum evaporation of the distillate of formic acid and water we also obtained 1.87 g of oil. The oily product crystallized on long standing. The yield of α-chloro-ω-sulfovaleric acid was established by titration of an aliquot portion of the oily product with alkali and was 30% of the theory. The bis-S-benzylisothiouronium salt $COOH-CHCl-(CH_2)_3SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2$ had m.p. 111 to 111.5° (after three recrystallizations from water). Found: C 45.56, 45.44; H 5.39, 5.24; Cl 6.90%. $C_{21}H_{29}O_5ClN_4S_3$. Calculated: C 45.94; H 5.29; Cl 6.47%.

Chlorination of $HCl \cdot NH_2(NH=)CS(CH_2)_3CH=CCl_2$. Through a solution of 5.5 g of the isothiourium chloride derivative (prepared from 1,1,5-trichloro-1-pentene) in 25 ml of anhydrous formic acid with stirring and a temperature of 35° was passed a stream of chlorine until evolution of hydrogen chloride stopped. After the reaction mixture had been treated with warm water, the product of addition of chlorine to the double bond precipitated as an oil and the α-chlorocarboxylic acid remained in solution. The oily layer was separated (1.5 g) and treated with a concentrated soda solution. We obtained 1.35 g of sodium salt $CCl_3-CHCl-(CH_2)_3SO_3Na \cdot H_2O$ (19% of the theory). Found: C 18.13, 17.95; H 2.98, 2.76%. $C_5H_9O_4Cl_4SNa$. Calculated: C 18.18; H 2.72%. The S-benzylisothiuronium salt had m.p. 150-151° (after three recrystallizations from water). A mixed sample with the analogous salt obtained in the previous experiment gave no melting point depression. The solution, which contained α-chloro-ω-sulfovaleric acid, was evaporated in a vacuum at 30-35°. The yield of acid was determined by alkali titration of an aliquot portion of the residue, and was 64.6%. The bis-S-benzylisothiuronium salt $[HOOCCHCl-(CH_2)_3SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2]$ had m.p. 111-111.5°, (after three recrystallizations from water). Found: C 45.63, 45.53; H 5.35, 5.32%. $C_{21}H_{29}O_5ClN_4S_3$. Calculated: C 45.94, H 5.29%. A mixed m.p. with the corresponding salt obtained in the previous experiment gave

Substances Obtained by Chlorination of $CCl_2=CH-(CH_2)_nSC(=NH)NH_2 \cdot HCl$ in Anhydrous Formic Acid.

n	Formula*	M. p., °C***	Found, %			Calculated, %			Yield, % of theory
			C	H	Cl	C	H	Cl	
3	$COOH-CHCl-(CH_2)_3SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2$	111—111,5	45,63 45,53	5,35 5,32		45.94	5,29		64,6**
	$CCl_3-CHCl-(CH_2)_3SO_3Na \cdot H_2O$	—	18,13 17,95	2,98 2,76		18,18	2,72		19
5	$COOH-CHCl-(CH_2)_5SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2$	132—133	47,43 47,55	5,61 5,74		47,86	5,72		58,3**
	$CCl_3-CHCl-(CH_2)_5SO_3Na \cdot H_2O$	—	22,87 22.97	3,53 3,40	39,07 39,04	23,46	3,63	39,38	15,7
7	$COOH-CHCl-(CH_2)_7SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2$	124—125	49,38 49,32	6,05 6,14		49,62	6,12		44,8**
	$CCl_3-CHCl-(CH_2)_7SO_3Na \cdot H_2O$	—	27,69 27.59	4,48 4,34	36,29 36,15	27,97	4,40	36,78	42
9	$COOH-CHCl-(CH_2)_9SO_3H \cdot 2C_6H_5CH_2SC(=NH)NH_2$	143	50,93 51,25	6,57 6,62		51,22	6,48		56,2**

*In this column we give the formula of the substances in the form in which the chlorination products were isolated and identified.

**The yield was determined by alkali titration of an aliquot portion of the crude α-chloro-ωsulfocarboxylic acid.

***It should be noted that the S-benzylisothiuronium salts obtained clearly showed the presence of alternating m.p. temperatures.

no m.p. depression. In an analogous way we carried out the chlorination of compounds with the general formula $CCl_2=CH-(CH_2)_nSC(=NH)NH_2 \cdot HCl$, where n = 5, 7, 9. The results are given in the table.

In the case where n = 9, the oily layer which precipitated when the reaction mixture was treated with water was the α-chlorocarboxylic acid [$COOH-CHCl(CH_2)_9SO_3H$]; tetrachloroundecylsulfoacid was not found in this experiment.

SUMMARY

1. We obtained α-chloro-ω-sulfocarboxylic acids [$COOH-CHCl-(CH_2)_nSO_3H$] by chlorination in a medium of anhydrous formic acid, along with isothiuronium salts with the structure $CCl_2=CH-(CH_2)_n \cdot SC(=NH)NH_2 \cdot HCl$, where n = 3, 5, 7, 9. In an analogous way, starting from dichloroalkenylsulfonates with the structure $CCl_2=CH-(CH_2)_nSO_3Na$ we have obtained the α-chloro-ω-sulfocarboxylic acids where n = 1, 3.

2. Along with the "coupled chlorination" of the above-mentioned substances, there has occurred addition of chlorine to the double bond with formation of substances with the structure $CCl_3-CHCl-(CH_2)_n-SO_3H$.

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SOLUTIONS OF AROMATIC ORGANIC LITHIUM COMPOUNDS IN ETHERS

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The stability of ether solutions of lithium organic compounds depends on the structure of the ethers and the RLi [1]. The most widely used medium for the synthesis of aromatic RLi is diethyl ether, in which these compounds are sufficiently stable. It is known that the reactivity of RLi varies greatly depending on the degree of association of these compounds and the character of the complex [1-3]. For example, complexes with lithium bromide lower the reactivity of RLi [4]. In the presence of a molecule of an electron donor, an ether [5], amine [6], sulfide [7], and some unsaturated compounds, the reaction of RLi is often sharply increased and even changes its direction. For example, in the polymerization of isoprene and n-butyl lithium in n-heptane there is obtained a polymer with a cis-1,4-structure with a yield of 90%, and in ether there are formed 1,2-, 3,4-, and trans-1,4-structures [5]. The addition of ether increases the rate of polymerization of divinyl by n-butyl lithium and raises the content of 1,2-sections in the polymer; the rate of copolymerization of divinyl and styrene is increased [8]. Polymerization of 1,3-butadiene by RLi has been described in [9]. Therefore, an explanation of the structure of the lithium organic compounds in various solvents is of great practical and theoretical value. The formation of complexes between the molecules of lithium organic compounds has been studied in several works [2,3]. The nature of these RLi complexes is apparently analogous to the similar complex compounds of R_2Be, R_3B, and R_3Al, and is connected with the formation of multicentered electron orbits [10]. The tendency of organic lithium compounds to association also determines the chief properties of these compounds. Organic lithium compounds can also give another type of complex with ether molecules, amines, etc. (molecules of electron donors). It is evident that the character and strength of such acceptor–donor complexes is also a reason for the sharp change in properties of the lithium organic compounds in ether solution.

The purpose of the present work was to explain the effect of ethers on the structure and character of the complexes of organic lithium compounds by infrared spectra [4]. We studied solutions of phenyl lithium, o-, m-, and p-tolyl lithium, p-chlorophenyl lithium, p-bromophenyl lithium [1,11], mesityl lithium, and fluorenyl lithium [12] in diethyl, di-n-propyl, diisopropyl, di-n-butyl, and diisoamyl ethers [11]. We also studied solutions of methyl lithium [1] and ethyl lithium [1,13] in the same ethers. The results of the study showed that on solution of the organic lithium compounds in ether there apparently began a deformation or splitting of the primary RLi complexes due to the dispersing and dipolar action of the ethers and then, depending on the structures of RLi and R_2O, there was formed a new complex between the molecules of ether and RLi (acceptor–donor). The increased reactivity of RLi in ether solution occurs in connection with the strengthened polarity of the bond C–Li in the complex of RLi with the ether. It is characteristic for this complex that in the infrared spectra of most of the solutions studied there were intense bands at about 1070 cm^{-1}, 900 cm^{-1}, and 560 cm^{-1}, which were apparently connected with the formation of etherates, since they were absent in the spectra of most of the crystalline samples. By analogy with the data which we recently obtained on the isotopic effect for aliphatic organic lithium compounds, and also on the basis of the ebulloscopic data in the literature [3], we can suggest that the band at about 560 cm^{-1} in the spectra of aromatic organic lithium compounds is related to the group C–Li, in the dimer formed by further association with the ether molecule.

This problem will be studied in more detail by isotopic substitution in the aromatic lithium organic compounds.

In this work we describe the synthetic part. We should mention that in the region of the infrared spectra which we studied (2000-650 cm^{-1}) we did not find much difference in the spectra of ether solutions of pure RLi (R = phenyl, tolyl, methyl) which did not contain LiBr, or ordinary ether solutions of RLi which contained equal amounts of LiBr. Hence, the formation of a ternary complex of RLi with the halide and diethyl ether actually was not shown in the spectral region studied.

For aromatic lithium organic compounds, besides the previously described ternary complexes 2RLi · LiBr · · $2(C_2H_5)_2O$ of phenyl lithium and tolyl lithium [14], we obtained complexes of the same composition for m-tolyl lithium. In the case of o-tolyl lithium, on prolonged cooling of a concentrated ether solution (2N for RLi and LiBr) to −80°, no ternary complex precipitated, nor was there a precipitate of the etherate of lithium bromide, which indicates the formation of a well-soluble complex. The same observation was made for a 1.5 N (for RLi and LiBr) solution of 2,5-dimethylphenyl lithium. Solutions of these aromatic compounds in diethyl ether were stable, which could explain the decreased reactivity of RLi due to complex formation with LiBr and ether. On concentration of the filtered ether solutions of the aromatic lithium organic compounds under nitrogen or argon, and evaporating dry in a vacuum, we could obtain a slightly colored, very active precipitate (RLi and LiBr in the ratio 1:1); it kept well sealed in an ampule under argon even up to a year, and could be used for reaction by suspending it in ether, in which a considerable part of the lithium bromide did not dissolve.

For a study of the complexes of aromatic lithium organic compounds in ether [1] we prepared a large amount of RLi by exchange reaction from aliphatic lithium organic compounds and aromatic RBr in n-hexane or benzene solution [11]. We showed that the RLi prepared by this method sometimes contained considerable admixtures of LiBr (3-25%) and formed solutions of RLi in ether with a small content of LiBr (5:1). We obtained such solutions with the ethers: diethyl, di-n-propyl, diisopropyl, di-n-butyl, diisoamyl, and tetrahydrofuran. The solutions usually had a light yellow color. The content of lithium bromide did not exceed that which would be found in solutions cooled from 0 to −25°, or by heating (from 35 to 60°). On solution in anisole the content of RLi:LiBr was 10:1. In the control experiments we prepared a 1 N solution in di-n-butyl ether for pure phenyl lithium which contained no halide salt, and heated at 50-60° with excess pure lithium bromide. The solution was 1 N to C_6H_5Li and 0.19 N to LiBr. On heating lithium bromide in di-n-butyl ether no solution occurred. Hence, in this case also we are dealing with complex formation. It is interesting to note that phenyl lithium, o-tolyl lithium, and p-tolyl lithium dissolve somewhat in dry chlorobenzene, forming a 0.1-0.05 N solution. The reaction with Michler's ketone by these solutions, without addition of ether, is positive. The Gilman test is preserved when the solutions stand under argon for 2-3 days. The solution does not contain lithium bromide. All the crystalline lithium organic compounds obtained in this study were used as catalysts for the polymerization of ethylene with $TiCl_4$ [15].

EXPERIMENTAL

All the work with solutions and precipitates of the lithium organic compounds was carried out with a slight positive argon pressure. We used pure and dry solvents. It is recommended to keep the solvents in flasks filled with argon and to remove with a siphon by argon pressure. Metallic lithium was cut into thin plates, freed from a film of oxide, and cut in a chamber under argon. The work was controlled by analysis [13,16]. All the work with organic lithium compounds as precipitates or in concentrated solutions required great attention and accuracy, since with small access of air the organic lithium compounds could explode. This had to be observed especially in obtaining crystalling ethyl lithium, p-chlorophenyl lithium, and p-bromophenyl lithium. The residues of the reaction mixtures with admixed metallic lithium in work on a large scale were best poured quickly into benzene (in an atmosphere of inert gas), and then poured into sand in an especially prepared place outside, and not decomposed in the laboratory. In work with the individual lithium organic compounds, during the synthesis, it was necessary to wear a protective mask of organic plastic, or the best goggles.

Preparation of a benzene solution of n-butyl lithium (from n-butyl chloride). The work was carried out under argon in a 1-liter apparatus. Filling the flask with solvent and introduction of lithium were carried out under the same conditions as for ethyl lithium [13]. We placed in a flask 400 ml of benzene and 12.4 g of lithium (1.5 + excess), heated it with stirring to 30-35°, added 4-5 ml of n-butyl chloride, and the remaining amount (altogether 70 g, 0.75 M) was diluted with 100 ml of benzene and added in the course of 2-3 hr, keeping the temperature of the reaction mixture at 50-55°. The reaction usually began immediately after adding the first portion of butyl chloride, as shown by warming, strong turbidity of the solution, and sinking of the pieces of lithium. At the end of butyl chloride addition, the mixture was stirred for 3 hr at 45-50°, 1 g of freshly cut lithium was added, and the mixture was stirred for another hour at 45-50°. Then the dropping funnel was replaced by the siphon and the solution was forced over by argon into a half-liter measuring cylinder. The yield of n-butyl lithium reached 75-80%. After settling, we obtained a clear, colorless solution, about 1.15-1.25 N.

If the reaction was carried out in the same apparatus, but using 13 g of lithium, 250 ml of benzene, and adding 70 g of butyl chloride (without dilution) during 3 hr, and stirring at 40-45° for 6 hr, we could obtain a 1.95-2.05 N solution of n-butyl lithium, but such a solution settled with more difficulty to clearness, and needed further

filtration. Therefore, if it was necessary to concentrate the n-butyl lithium solution, it was better to start from a 1 N solution and concentrate it.

Preparation of a hexane solution of n-butyl lithium. The work was carried out in an apparatus with 1-liter capacity. In a flask with a stream of argon was placed 500 ml of hexane, 7 g of lithium (cut very fine under argon), a stirrer was inserted, and the solution was brought to strong boiling. To the boiling solution in the course of 3-4 hr was added evenly 37.0 g (0.4 M) of n-butyl chloride in 30 ml of hexane. It was stirred further for 1 hr with boiling, one more g of freshly cut lithium was added, and stirring and boiling were continued for 2 hr more. Then the solution was filtered and siphoned by argon pressure into a vessel filled with argon. The filter for the apparatus with ordinary (not dense) filter paper was dried in a desiccator over phosphorus pentoxide. We obtained a perfectly clear and colorless 0.7-0.8 N solution of n-butyl lithium with a yield of 87-95%. Increased amounts of reacting substances could give a 1.5-2 N solution of n-butyl lithium. The residue in the flask was treated with benzene and decomposed in the same way as in preparing ethyl lithium. The apparatus for filtration was rapidly disconnected in a stream of argon, the lower part was closed off and transferred under pressure, and the cover was raised for immediate removal of the filter with a large pipet. There should be nothing easily inflammable nearby, since the filter usually catches fire immediately; if it is taken out slowly, it catches fire in the funnel.

We can obtain a hexane solution of n-propyl lithium, n-amyl lithium, n-hexyl lithium, n-heptyl lithium, n-decyl lithium, n-dodecyl lithium, and n-hexadecyl lithium under exactly the same conditions. The yield varies from 75-80 to 85-97%, depending on the purity of the starting n-alkyl chloride and the accuracy of the work. As a rule, the resulting hexane solutions are perfectly colorless and clear, and can be kept for a long time without decomposition under argon (see [17]).

Preparation of crystalline phenyl lithium mixed with lithium bromide. In the usual apparatus for carrying out the exchange reaction [11], with capacity 500 ml, we placed 250 ml of 1.03 N colorless and clear hexane solution of n-butyl lithium (16 g, 0.25 M) and added 39 g (0.25 M) of freshly distilled bromobenzene. After mixing, the solutions remained clear for 15-20 min; then a snow-white precipitate of phenyl lithium began to come down; the solution stood at room temperature overnight; on the next day the white, pasty mass was diluted with 100-150 ml of dry hexane, stirred, and filtered as described in the case of ethyl lithium. The precipitate filtered very easily; it was washed 3-4 times by sucking through small portions of pure hexane and dried in a vacuum for 3-4 hr, releasing the vacuum with argon. We obtained about 25 g of phenyl lithium which was put up in sealed ampules of the desired weight; we opened three ampules for analysis. We determined the content of lithium bromide and the lithium content. The content of lithium in the resulting phenyl lithium was usually close to the calculated value, considering the admixed lithium bromide. For example, in samples of 0.0962, 0.1315, and 0.0865 the lithium content was 7.28, 7.49, and 7.44%, respectively, with subtraction for the admixture of LiBr, 8.12, 7.91, and 8.03%, respectively. By calculation for C_6H_5Li the lithium content was 8.27%.

The yield of pure phenyl lithium was about 20 g, that is, 85-87%; admixed lithium bromide was 10-15% (5 to 10 g). We could also carry out the preparation of phenyl lithium in larger quantities; the apparatus used had correspondingly greater volume. The preparation of crystalline phenyl lithium from a benzene solution of ethyl lithium, as we previously described [11], or using a benzene solution of n-butyl lithium, was less satisfactory in work with larger quantities, since the resulting precipitate was more difficult to filter and wash.

Preparation of a solution of phenyl lithium in di-n-butyl ether. We took about 30 g of phenyl lithium with an admixture of 11% lithium bromide (see above) and dissolved it under argon in 250 ml of di-n-butyl ether. The mixture was filtered to give a light-golden, perfectly clear solution which analyzed for 1.31 N phenyl lithium and 0.201 N lithium bromide. On prolonged cooling of this solution to −80° no turbidity or precipitation was observed. The solution of phenyl lithium in dibutyl ether can be used in those cases where it is necessary to carry out a reaction at higher temperatures. In the same way we obtained solutions in dibutyl ether of p-tolyl lithium, m-tolyl lithium, o-tolyl lithium, or α-naphthyl lithium (from the etherate).

Preparation of a solution of pure phenyl lithium in di-n-butyl ether. 5 g of phenyl lithium which contained no admixture (obtained by the exchange reaction from triphenyl antimony) was dissolved in 60 ml of di-n-butyl ether and filtered from a small amount of precipitate. The solution was clear and light yellow; it analyzed for 1.01 N phenyl lithium and contained no halide. On long cooling to −80° no precipitate appeared.

Preparation of lithium bromide from lithium bromide dioxanate. We took 8.2 g of lithium bromide dioxanate and 100 ml of freshly prepared bromobenzene. More than half the solvent was distilled off under nitrogen; the

remaining precipitate was sucked off under nitrogen, washed with hexane and three times with pentane, and dried in a vacuum with warming to 45-50°. The weight of the precipitate was 4 g. Found: Br 92.09, 92.14%; calculated for LiBr, Br 92.05%.

Solution of phenyl lithium in di-n-butyl ether and lithium bromide. Under nitrogen we took 30 ml of 1.01 N solution of phenyl lithium (free from lithium bromide) in n-butyl ether; to it we added 2.5 g of pure lithium bromide. The mixture was heated to 50-60° for 2 hr and filtered under nitrogen. By analysis, the solution contained 1 N phenyl lithium and 0.195 N lithium bromide. In a control experiment we heated 1.0 g of lithium bromide in 40 ml of di-n-butyl ether for 2 hr at 50-60°, and finally brought it to boiling; the solution was filtered hot. This solution did not contain lithium bromide. When we dissolved lithium bromide etherate, LiBr · 1 ether in dibutyl ether, after short standing precipitation of pure lithium bromide began.

Preparation of m-tolyl lithium from n-butyl lithium in hexane. We took 300 ml of 1.14 N solution of n-butyl lithium in hexane (20.8 g) and added 57 g of m-bromotoluene. The colorless solution took on a golden yellow color; there was no heating. The white precipitate of m-tolyl lithium appeared after standing overnight, filling the entire volume of the solution. We added 200 ml of dry hexane, stirred the precipitate, filtered, washed three times with hexane (100 ml), and dried for 3 hr in a vacuum. All the operations were carried out in argon; for the apparatus, see above. The admixture of lithium bromide was 17.5% (4.2 g); yield of m-tolyl lithium 60% (20 g). Analysis with subtraction of lithium bromide: Li 6.88, 6.92%; by calculation, 7.08% Li.

Preparation of the ternary complex of m-tolyl lithium with lithium bromide and ether. We took 25 g of precipitate which contained 20 g of tolyl lithium and 5 g of lithium bromide (prepared as above), and dissolved them in 200 ml of 1.3 N ether solution of lithium bromide. The solution was filtered free of turbidity, the clear filtrate was cooled to −15°; large needle-shaped crystals precipitated. The crystals were quickly sucked off and dried in a stream of argon until loose (3 hr). A sample of 0.6066 and 0.7736 M contained, respectively: RLi 44.98, 45.34%; LiBr 19.49, 18.46%; ether by difference 35.53, 36.02%.

The composition of the resulting complex was $2m\text{-}CH_3C_6H_4Li \cdot 1LiBr \cdot 2$ ether. A complex of the same composition separated from a solution obtained by the action of lithium on m-bromotoluene under the usual conditions. The starting solution was 0.75 N on RLi and 0.8 N on lithium bromide. The crystals of the ternary complex precipitated on cooling to −15°.

Preparation of o-tolyl lithium from n-butyl lithium in hexane. We took 140 ml of 1.16 N hexane solution of n-butyl lithium (10.4 g) and added 27.6 g of o-bromotoluene; a light yellow color appeared, there was no heating, the solution was clear. A precipitate came down on standing overnight. We added 100 ml more of hexane; the precipitate was stirred and filtered. It was washed on the filter four times with n-hexane and dried in a vacuum. Admixed lithium bromide was 8%, yield of o-tolyl lithium was about 12 g (75%). With subtraction of the admixed lithium bromide, analysis for Li gave 6.99, 6.95%; calculated for C_7H_7Li, 7.08%. The reaction could be carried out with double or triple amounts.

We could not separate a ternary complex of composition 2RLi · 1LiBr · 2 ether from o-tolyl lithium. Even from a solution 2 N for RLi and 2 N for LiBr with prolonged cooling to −75°, there was no precipitate of a complex or an etherate of LiBr; that is, this complex had much greater solubility.

Preparation of p-tolyl lithium from n-butyl lithium in hexane. The reaction was carried out with 210 ml of 1.16 N hexane solution of n-butyl lithium (15.6 g, 0.24 M) and 41.4 g of p-bromotoluene (0.24 M), dissolved in 50 ml of n-hexane. After mixing, the solution was clear, almost colorless; there was no heating. This reaction did not always take place in one day; sometimes, the reaction mixture was left standing for two days. The white precipitate of p-tolyl lithium was filtered off, washed four times with n-hexane, and dried in a vacuum (2 hr). The yield of p-tolyl lithium was 80% (19.2 g). The admixture of lithium bromide varied from 7 to 15%. Analysis with subtraction of the lithium bromide gave good results: 6.82-6.88% Li; by calculation, 7.08% Li.

Preparing p-chlorophenyl lithium. Crystalline p-chlorphenyl lithium was not obtained in large amounts, since with small access of air (mixed with nitrogen or argon) there was rapid explosion. In a single operation we could obtain not more than 10 g of p-chlorophenyl lithium.

In the apparatus under argon we placed 115 ml of benzene solution of ethyl lithium (containing 3.15 g of ethyl lithium), and to it we added an equimolecular amount of p-chlorobromobenzene (16.7 g) in 25 ml of benzene; it stood overnight at room temperature. The yellow crystals which separated were filtered off under argon, washed

three times with n-hexane, and dried in a vacuum. Yield 5-7 g (50-60%); admixed lithium bromide from 1.5 to 8%. By analysis with subtraction of the lithium bromide: Li 5.61, 5.57%; calculated for ClC_6H_4Li, Li 5.86%.

Preparation of p-bromophenyl lithium. The preparation of p-bromophenyl lithium could also not be carried out with large quantities, because of the danger of explosion [18]. We took 100 ml of 0.66 N solution of ethyl lithium in benzene (2.4 g) and with cooling to 0° added under argon an equimolecular amount of p-dibromobenzene (15.4 g) in 35 ml of benzene. After standing for a night, the precipitate which separated was filtered under argon, washed three to four times with n-hexane, and dried in a vacuum. Yield of p-bromophenyl lithium 75-80%; admixture of lithium bromide from 1.5-5%. Analysis with subtraction of lithium bromide: Li 4.10, 4.15%; by calculation for BrC_6H_4Li, Li 4.28%.

Method for obtaining solutions of organic lithium compounds in different ethers. Usually a sample of 4-5 g of aromatic organic lithium compound, pure or containing a mixture of lithium bromide or 0.5 g of ethyl lithium or methyl lithium, was dissolved under argon in 20-25 ml of the corresponding ether. The solution was filtered under argon to remove turbidity or precipitate (lithium bromide) through a pleated filter in a small filtration apparatus [11]. The freshly prepared solution was quickly used for determination of the infrared spectrum, and we made a parallel analysis of the solution for lithium and halogen.

When heating was observed in preparing the solution, the filtered solution was removed and analyzed, but then a second solution was prepared in which solution was carried out at 0° or at a lower temperature. The second solution was also removed and analyzed. In other cases, the solution was deliberately prepared by allowing heating to 40-50° or higher, or by warming it to this temperature (see [1]).

If a large amount of lithium organic compound was sealed in an ampule, it was put in with a stream of argon at about 4-5 g of the substance. Removal of the substance from the ampule into the apparatus for solution was carried out as follows: a nozzle was made on the side where the ampule was to be connected; it was closed with blowing through of argon. A ring of soft red rubber was put on the ampule so that it fitted exactly on the nozzle, and wax was removed from the end of the ampule. The ampule, filled with argon, was opened in the vertical position and the nozzle was immediately placed in it with a stream of argon passing [11]. Then the end of the nozzle was disconnected and sunk 4-5 cm into the neck of the apparatus, with a counter current of argon passing through the nozzle and through the apparatus. The precipitate was transferred either into the empty apparatus and the ether was added later, or was put directly into the cooled ether. The apparatus was closed, shaken for solution, and the solution was then filtered through a pleated filter into a small filtration apparatus; after several minutes the sample was removed and rapidly used for measurement and analysis. Samples of the solution were transferred by a pipet filled with argon into an apparatus also filled with argon.

SUMMARY

1. We have described a method for synthesis of aromatic organic lithium compounds in hexane solution.

2. We have studied ether solutions of aromatic and aliphatic organic lithium compounds by infrared spectra.

3. We have observed intense bands in the region 560 cm^{-1}, 900 cm^{-1}, and 1070 cm^{-1}, characteristic for etherates of ArLi.

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SUBSTITUTION REACTIONS OF A MERCURY ATOM COMBINED WITH A SATURATED CARBON ATOM, BY HALIDES

COMMUNICATION 2. REACTION OF BENZYLMERCURY CHLORIDE WITH IODINE IN THE PRESENCE OF IODINE ION IN DIMETHYLFORMAMIDE, METHANOL, AND ETHANOL

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A study of the kinetics of the reaction

$$C_6H_5—CH_2HgCl + I_2\,(CdI_2) \rightarrow C_6H_5—CH_2I + HgClI + CdI_2$$

in 70% dioxane and in the presence of an excess of iodine ions, using cadmium iodide [1] as the starting material, was reported in a previous communication. As an extension of the study of electrophilic substitution mechanism on a saturated carbon atom, the effect of solvent on the rates of those reactions was studied. Dimethylformamide,* methanol, and ethanol** were used as the solvents.

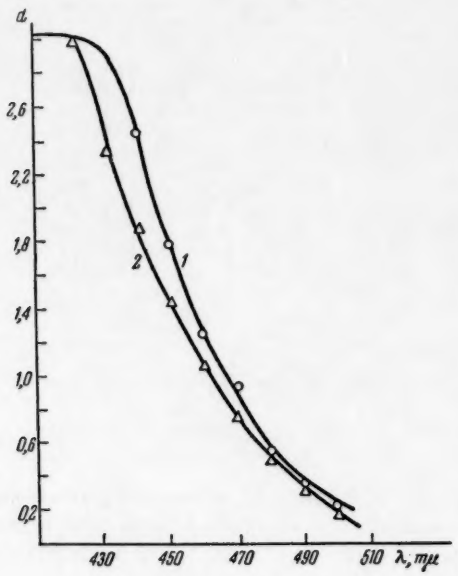


Fig. 1. Standardized curves d = $f(\lambda)$ for iodine solution concentration $2 \cdot 10^{-3}$ M/liter in the presence of cadmium iodide of $2 \cdot 10^{-2}$ M/liter concentration, in dimethylformamide (1) and methanol (2).

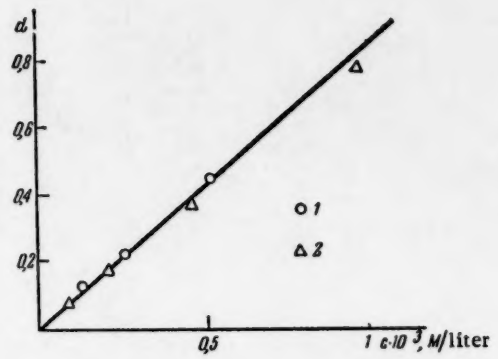


Fig. 2. Standardized curves d = $f(c)$ for iodine solutions in the presence of cadmium iodide in dimethylformamide (1) and methanol (2).

The reaction kinetics were investigated spectrophotometrically on an SF-4 spectrophotometer by studying changes in the optical density of iodine. The other products, starting and final, do not absorb in that region. Standardized curves d = $f(\lambda)$ for iodine solutions in the

* Dimethylformamide was purified by shaking with alkali, followed by vacuum distillation.
** Methanol and ethanol were dehydrated by the method given in [2].

TABLE 1. Dimethylformamide

t 20° c_0 1·10⁻³ M/liter		t 20° c_0 0,5·10⁻³ M/liter		t 15° c_0 1·10⁻³ M/liter		t 25° c_0 1·10⁻³ M/liter	
τ, min	d	τ, min	d	τ, min	d	τ, min	d
1,75	0,790	2,0	0,452	1,75	0,815	1,5	0,839
10,0	0,739	12,5	0,428	7,5	0,764	6,0	0,769
16,5	0,689	22,0	0,398	15,5	0,732	10,5	0,718
22,5	0,640	32,0	0,381	26,5	0,663	18,5	0,626
29,25	0,604	43,25	0,357	37,75	0,619	24,5	0,573
38,0	0,560	55,0	0,339	52,75	0,568	31,75	0,520
50,0	0,503	65,5	0,320	65,0	0,526	40.25	0,471
64,25	0,456	83,0	0,295	75,5	0,509	47,0	0,437
75,0	0,426	102,25	0,274	87,0	0,470	57,0	0,398
85,25	0,398	120,5	0,255	98,5	0,447	65,5	0,367
97,75	0,370	145,75	0,235	113,0	0,421		
107,25	0,352	165	0,219	125,25	0,406		
118,5	0,334	184	0,210	139,75	0,376		
128.0	0,316			154,5	0,359		
K_2=0,203 $\frac{\text{liter}}{M\cdot\text{sec}}$		K_2=0,236 $\frac{\text{liter}}{M\cdot\text{sec}}$		K_2=0,142 $\frac{\text{liter}}{M\cdot\text{sec}}$		K_2=0,347 $\frac{\text{liter}}{M\cdot\text{sec}}$	

TABLE 2. Methanol

t=20° c_0=1·10⁻³ M/liter		t 20° c_0=0,5·10⁻³ M/liter		t=15° c_0=1·10⁻³ M/liter		t=24° c_0=1·10⁻³ M/liter	
τ, min	d	τ, min	d	τ, min	d	τ, min	d
2,0	0,742	2,0	0,288	1,5	0,728	1,75	0,715
6,0	0,605	6,0	0,265	3,16	0,662	3,75	0,660
9,33	0,540	11,16	0,246	7,75	0,610	6,16	0,561
12,0	0,496	16,0	0,218	12,0	0,550	8,83	0,512
14,5	0,457	21,25	0,201	15,75	0,503	11,83	0,452
17,5	0,422	29,25	0,174	21,33	0,451	15,0	0,415
20,5	0,385	34,16	0,169	25,0	0,419	17,5	0,375
23,66	0,357	41,33	0,143	30,25	0,383	21,75	0,332
26,25	0,336	46,33	0,131	36,75	0,348	25,25	0,309
29,33	0,312	50,75	0,124	43,66	0,311	29,75	0,271
34,66	0,283	54,16	0,115	49,5	0,284	36,0	0,254
39,0	0,259			57,75	0,261		
				63,0	0,244		
K_2=0,800 $\frac{\text{liter}}{M\cdot\text{sec}}$		K_2=0,814 $\frac{\text{liter}}{M\cdot\text{sec}}$		K_2=0,575 $\frac{\text{liter}}{M\cdot\text{sec}}$		K_2=0,951 $\frac{\text{liter}}{M\cdot\text{sec}}$	

presence of cadmium iodide and at iodine concentration of $2 \cdot 10^{-3}$ M/liter for all solvents are given in Fig. 1. For the measurements we selected λ 470 mμ. The reaction was conducted with equimolar reagent ratios in the interval of iodine concentrations and benzylmercury chloride concentration of $(0.5\text{-}1) \cdot 10^{-3}$ M/liter. The concentration of cadmium iodide was $1 \cdot 10^{-2}$ M/liter.

Within the interval of concentrations mentioned the solutions of iodine in the presence of cadmium iodide in all solvents obey the Lambert-Beer law: $d = \epsilon c l$, where d is the optical density, c is the concentration, l is the length of cuvette, ϵ is molar absorption coefficient (Fig. 2), and thus the ratio c_0/c can be replaced by the ratio of corresponding optical densities. The reaction kinetics were studied at 15, 20, and 25°.

EXPERIMENTAL

To a thermostatically kept solution of iodine was added, under stirring, a solution of benzylmercury chloride previously maintained at the same temperature. The beginning of the reaction was assumed to be the moment of addition of the second reagent. Samples were taken at predetermined intervals, and their optical densities were measured.

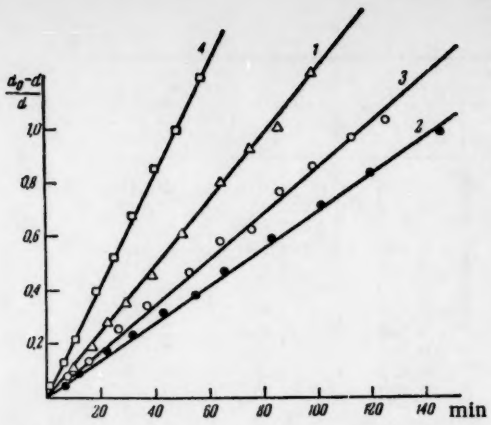


Fig. 3. Graphs of the ratio $(d_0 - d)/d$ against τ for reactions in dimethylformamide, relating to experiments 1, 2, 3, 4.

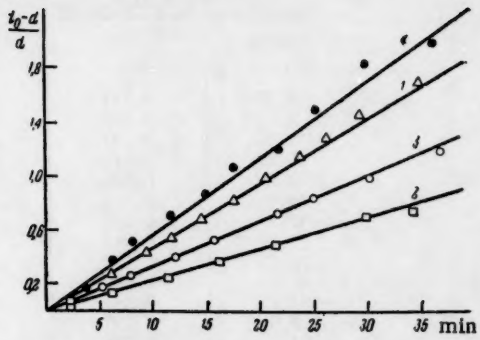


Fig. 4. Graphs of the ratio $(d_0 - d)/d$ against τ for reactions in dimethylformamide, relating to experiments 1, 2, 3, 4.

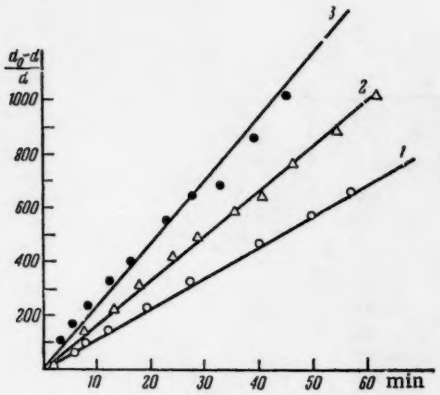


Fig. 5. Graphs of the ratio $(d_0 - d)/d$ against τ for reactions in ethanol, relating to experiments 1, 2, and 3.

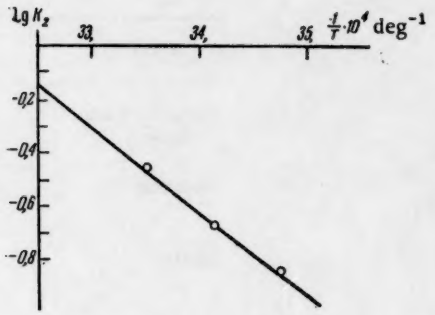


Fig. 6. Graph of the dependency of $\log K_2$ on $1/T$ for dimethylformamide.

The experimental data on changes in optical density of the solution in time are given in Tables 1, 2, and 3* for dimethylformamide, methanol, and ethanol, respectively.

The rate constant of the reaction is properly expressed by the equation

$$K_2 = \frac{1}{c_0 \tau}\left(\frac{c_0}{c} - 1\right)$$

Graphic representation within the coordinates $[(d_0 - d)/d] - \tau$ (Figs. 3, 4, and 5) illustrates convergence in the values of constants of second-order reactions for different initial concentrations of reagents at constant temperature in solvents under investigation.

Table 4 gives the values of rate constants of the second-order reactions for dimethylformamide, methanol, and ethanol, obtained at various temperatures, their logarithms, corresponding absolute temperatures, and their inverse magnitudes. Figures 6, 7, and 8 give the graphs of dependencies of the logarithm of the reaction rate on the inverse temperature for dimethylformamide, methanol, and ethanol.

* d_0 is most accurately determined by extrapolation of the kinetic curve to $\tau = 0$.

TABLE 3. Ethanol

$t=15°$ $c_0=1\cdot10^{-3}$ M/liter		$t=20°$ $c_0=1\cdot10^{-3}$ M/liter		$t=25°$ $c_0=1\cdot10^{-3}$ M/liter	
τ, min	d	τ, min	d	τ, min	d
4,83	0,791	1,5	0,822	1,0	0,741
7,66	0,762	4,5	0,760	3,25	0,687
12,16	0,731	7,5	0,732	5,5	0,650
19,25	0,679	13,16	0,682	8,58	0,616
27,0	0,630	17,66	0,638	12,5	0,572
40,0	0,571	24,0	0,589	16,58	0,544
49,5	0,530	28,5	0,561	23,0	0,488
57,16	0,503	35,25	0,525	27,66	0,462
72,5	0,452	40,33	0,506	32,5	0,448
83,75	0,430	46,0	0,471	38,75	0,406
104,0	0,385	54,25	0,440	40,75	0,375
118,0	0,356	61,75	0,410	49,75	0,359
137,5	0,321	72,75	0,380	54,58	0,345
		84,33	0,350	59,0	0,341
				65,75	0,309
$K_2=0,189\frac{\text{liter}}{M\cdot\text{sec}}$		$K_2=0,278\frac{\text{liter}}{M\cdot\text{sec}}$		$K_2=0,375\frac{\text{liter}}{M\cdot\text{sec}}$	

TABLE 4.

Solvent	T, °C	$1/T\cdot10^4$	K_2, $\frac{\text{liter}}{\text{M}\cdot\text{sec}}$	$-\lg K_2$
Dimethylformamide	288	34,7	0,142	0,849
	293	34,1	0,215	0,668
	298	33,5	0,347	0,460
Methanol	288	34,7	0,575	0,250
	293	34,1	0.807	0,093
	297	33,6	0,951	0,022
Ethanol	288	34,7	0,189	0,724
	293	34,1	0,279	0,556
	298	33,5	0,375	0,426

Parameters of the Arrhenius equation were calculated from the data obtained. Table 5 gives the magnitudes of activation energies, entropy of the transitory composition, and logarithms of exponents of the reaction in various solvents.

For the sake of comparison, constants of reaction rates obtained at 20°, and corresponding data for the reaction in 70% dioxane, are also given. It can be seen from the experimental data obtained that the reaction rates in solvents under study fall into the series:

methanol > 70% dioxane > ethanol > dimethylformamide

and that the activation energies and entropies of the transitory composition decrease correspondingly. Should the rate of the process be determined only by the polarity of the medium, then the series should read differently:

dimethylformamide > methanol > ethanol > 70% aqueous dioxane

in accord with the electrical constants of the solvents. We assume that, in the given case, the determining effect on the reaction course is not only the polarity of the medium, i.e., solvation of the transitory composition, but also the ability of the solvent molecules to form complexes with the initial ($C_6H_5CH_2HgCl$) and final (HgICl) products. When we keep in mind that the attacking agent in all solvents is the same – the complex of I_2 with CgI_2, then it is obvious that the difference is only in the complex formation (or solvation at the limits of complex formation) of the molecules of the initial benzylmercury chloride

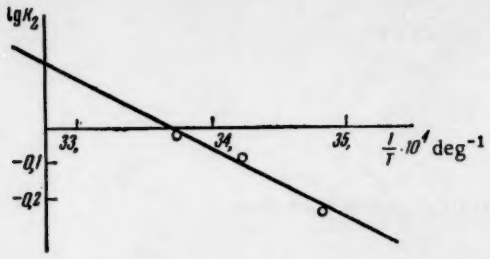


Fig. 7. Graph of the dependency of $\log K_2$ on $1/T$ for methanol.

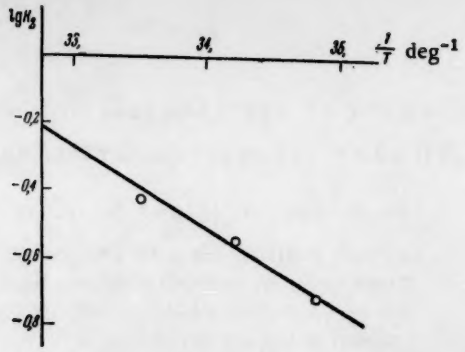
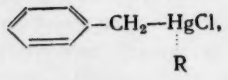


Fig. 8. Graph of the dependency of $\log K_2$ on $1/T$ for ethanol.



(where R is a solvent molecule), which then leads to the weakening of the C–Hg bond. It is known that aqueous dioxane is a highly complex forming substance, and thus the rate in it is much greater than in other solvents, despite the low dielectric permeability, equal to 18. When the complex-forming properties of solvents are about the same, i.e., in the case of compounds belonging to the same class as is the case with methanol and ethanol, the reaction rate will be determined by the polarity of the medium, which fully agrees with experimental data. Dimethylformamide is a less complex-forming substance than are oxygeneous solvents and, therefore, the reaction rates in it are relatively low, despite the fact that its dielectric constant is relatively high (36.5).

TABLE 5.

Solvent	E, kcal/M	log A	Δ S, entropy units at 20°	K_2 at 20°, liter/M · sec
Dimethylformamide	15.3	11.1	– 7.8	0.215
Methanol	9.6	7.1	–26.0	0.807
Ethanol	11.6	8.6	–19.6	0.279
70% Dioxane	10.8	7.7	–23.3	0.366

The dependency of the activation energy on the activation entropy in the reaction of benzylmercury chloride with iodine in an excess of cadmium iodide, in the solvents studied, is strictly linear, i.e., the compensation effect has taken place.

SUMMARY

1. We studied the reaction kinetics of benzylmercury chloride with iodine in an excess of CdI_2 in dimethylformamide, methanol, and ethanol.

2. In all solvents the over-all reaction order was two. Reaction rate constants of the second order were determined at various temperatures.

3. Parameters of the Arrhenius equation and activation entropies were found.

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2. "Preparative Organic Chemistry" [in Russian] (Moscow, 1959) pp. 156-157.

REACTION OF ARYL(ALKYL)AMINOMETHYLETHOXYSILANES WITH ALKYL(ARYL)HYDROXYSILANES

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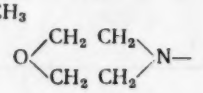
The literature describes a reaction where an ethoxy group on silicon is replaced by a triethyl (propyl)siloxy group on reaction of methylethoxysilanes with triethyl- and tripropylhydroxysilane in the presence of a catalyst – sodium silanolate [1,2]. The reaction also takes place on prolonged heating of trimethylethoxysilane with diphenyl dihydroxysilane [3]. In this work we studied the reaction of aryl(alkyl)aminomethylethoxysilanes with triethylhydroxysilane, dimethylphenylhydroxysilane, and with diethyldihydroxysilane. The study of this reaction showed that the introduction of an amino group in the α-position to a silicon atom in an organic radical enhances the reactivity of the alkoxy group in the exchange to the triethyl- or dimethylphenylsiloxy group. No catalyst is needed for the reaction, and it proceeds smoothly according to the following scheme:

$$XCH_2CH_3Si(OC_2H_5)_2 + 2(C_2H_5)_3SiOH \rightarrow (C_2H_5)_3SiO-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2X}{\overset{|}{\underset{|}{Si}}}}-Si(C_2H_5)_3 + 2C_2H_5OH,$$

where X = C_6H_5NH-, $(C_2H_5)_2N-$, ClC_6H_4NH-,  .

When the reagents of the reaction between diethylaminomethyl(methyl)diethoxysilane and triethylhydroxysilane were poured together at room temperature, the mixture heated up. When the reaction mixture was gradually heated to 150° over a period of 1 hr, more than 70% alcohol distilled off. Fractionation of the products yielded 1,1,1,3,3,3-hexaethyl-2-methyl-2-diethylaminomethyltrisiloxane in 78.5% yield. The reaction between phenylaminomethyldimethylethoxysilane and dimethylphenylhydroxysilane also proceeds well. During the first hour of heating of the reaction mixture already more than 70% of alcohol was formed, and 1,1,2,2-tetramethyl-1-phenylaminomethyl-2-phenyldisiloxane was obtained according to the scheme:

$$C_6H_5NHCH_2(CH_3)_2SiOC_2H_5 + C_6H_5(CH_3)_2SiOH \rightarrow$$
$$\rightarrow C_6H_5NHCH_2(CH_3)_2SiOSi(CH_3)_2C_6H_5 + C_2H_5OH.$$

In the instances studied, the substitution of alkoxy groups by a triethyl- or dimethylphenylsiloxy group proceeds easily, whether one or two ethoxy groups are being substituted.

The reaction of phenylaminomethyldimethylethoxysilane with diethyldihydroxysilane proceeds in a much more complicated way. Two products were obtained from that reaction: 1,1,3,3-tetramethyl-2,2-diethyl-1,3-di(phenylaminomethyl)trisiloxane and bis(phenylaminomethyl)tetramethyldisiloxane. The reaction proceeds not only according to the scheme:

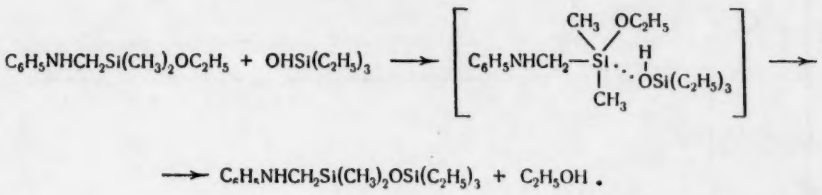
$$2C_6H_5NHCH_2(CH_3)_2SiOC_2H_5 + (C_2H_5)_2SiOH \rightarrow$$
$$\rightarrow C_6H_5NHCH_2(CH_3)_2SiO\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_2H_5}{\overset{|}{\underset{|}{Si}}}}-OSi(CH_3)_2CH_2NHC_6H_5 + 2C_2H_5OH,$$

but also has side reactions. Among those processes, the condensation of diethyldihydroxysilane

$$(C_2H_5)_2Si(OH)_2 \rightarrow HOSi(C_2H_5)_2—O—Si(C_2H_5)_2OH + H_2O$$

should be pointed out. The water which forms hydrolyzes the phenylaminomethyldimethylethoxysilane, which is followed by condensation of the hydrolysis product to bis(phenylaminomethyl)tetramethyldisiloxane.

As a result of these reaction studies, new compounds were obtained, which are represented in the table. The substitution reaction of an alkoxy group by a triethyl- and dimethylphenyloxy group is a nucleophilic substitution reaction. The ease of the exchange of the ethoxy group in aminomethylethoxysilanes for trialkyloxy groups is connected with the inductive effect of the nitrogen in the methyl radical on the silicon. Due to the inductive effect of the nitrogen, the silicon becomes more positive, and thus more easily undergoes the nucleophilic attack of trialkyl-(aryl)hydroxysilanes. The reaction mechanism can be expressed by the following scheme:



$$\longrightarrow C_6H_5NHCH_2Si(CH_3)_2OSi(C_2H_5)_3 + C_2H_5OH.$$

EXPERIMENTAL

1,1-Dimethyl-1-phenylaminomethyl-2,2,2-triethyldisiloxane (I). Into a flask provided with a stirrer, thermometer, and reflux condenser, was placed 13.7 g (0.068 M) freshly distilled phenylaminomethyldimethylethoxysilane and 9 g (0.68 M) freshly distilled triethylsilanol. The reaction mixture was heated for two hours with stirring, and the temperature was slowly raised to 170°. Only when the temperature in the reaction flask reached 85-90° did the formation of alcohol begin. After 2 hr of heating, 2 g (65%) of alcohol was distilled off, boiling point 78-80°, $n^{20}D$ 1.3640. The rest was vacuum distilled and yielded 16.3 g of a product boiling at 122-125° (1 mm); yield 84.5%. After repeated distillation, b.p. 109-109.5° (0.5 mm). Constants of the compounds obtained are given in the table. Found: C 60.96, 60.63; H 9.96, 9.86; Si 18.98, 18.79; N 4.93, 5.06%. $C_{15}H_{29}Si_2N_2O_1$. Calculated: C 60.93; H 9.89; Si 19.00; N 4.63%.

1,1,1,3,3,3-Hexaethyl-2-phenylaminomethyl-2-methyltrisiloxane during heating (III). Analogously, heating of 8.5 g (0.036 M) phenylaminomethyldiethoxysilane and 9.5 g (0.072 M) triethylsilanol for 1 hr yielded a distillate of 2.7 g (80%) alcohol. Distillation yielded 10.3 g of a product boiling at 150-165° (1 mm); yield 71%. After repeated distillation, b.p. 145-150° (0.5 mm) (see table). Found: C 58.54, 58.39; H 9.93, 9.94; Si 20.34, 20.54; N 3.9, 4.1%. $C_{20}H_{41}Si_3NO_2$. Calculated: C 58.34; H 10.04; Si 20.47; N 3.0%.

1,1,1,3,3,3-Hexaethyl-2-diethylaminomethyl-2-methyltrisiloxane (IV). Analogously, heating of 8.5 g (0.064 M) triethylsilanol and 7.0 g (0.032 M) diethylaminomethylmethyldiethoxysilane yielded 9.8 g of a product boiling at 105-115° (1 mm); yield 78.5%. After repeated distillation, b.p. 102-106° (1 mm) (see table). Found: C 55.36, 55.28; H 11.47, 11.45; Si 21.59, 21.70; N 3.97, 3.82%. $C_{18}H_{45}Si_3NO_2$. Calculated C 55.17; H 11.57; Si 21.51; N 3.57%.

1,1,1,3,3,3-Hexaethyl-2-morpholylmethylmethyltrisiloxane (V). Analogously, 8.5 g (0.064 M) of triethylsilanol and 7.3 g (0.031 M) morpholylmethylmethyldiethoxysilane yielded 9.5 g of a product boiling at 132;135° (1 mm); yield 74.6%. After repeated distillation, b.p. 129-131° (1 mm) (see table). Found: C 53.14, 53.19; H 10.51, 10.76; Si 21.00; 21.06; N 4.1%. $C_{18}H_{43}Si_3NO_2$. Calculated: C 53.28; H 10.68; Si 20.77; N 3.45%.

1,1,1,3,3,3-Hexaethyl-2-chlorophenylaminomethylmethyltrisiloxane (VI). Analogously, 8 g (0.029 M) of chlorophenylaminomethylmethyldiethoxysilane and 7.9 g (0.05 M) triethylsilanol yielded 6.3 g of a product boiling at 160-170° (2 mm); yield 48%. After repeated distillation, b.p. 151-153° (0.5 mm) (see table). Found: C 54.07, 54.17; H 8.92, 9.04; Si 18.42; N 4.0%. $C_{20}H_{40}Si_3NO_2Cl$. Calculated: C 53.86; H 8.98; Si 18.89; N 3.14%.

1,1,2,3,3-Pentamethyl-1,3-diphenyl-2-phenylaminomethyltrisiloxane (VII). Analogously, when 4.7 g (0.03 M) of dimethylphenylsilanol and 4.2 g (0.015 M) phenylaminomethylmethyldiethoxysilane reacted, the yield was 2 g of a product boiling at 187-195° (1 mm) (see table). Found: C 63.74, 63.74; H 7.29, 7.13; Si 18.58, 18.37; N 3.88%. $C_{24}H_{33}Si_3NO_2$. Calculated: C 63.80; H 7.36; Si 18.65; N 3.1%.

Reaction of Aryl(alkyl)aminomethylethoxysilanes with Alkyl(aryl)hydroxysilanes.

Name of substance	Formula of compound obtained	B.p., °C (mm Hg column)	Yield, %	n_D^{20}	d_4^{20}	MR	
						found	calculated
I	$(C_2H_5)_3SiOSi(CH_3)_2CH_2NHC_6H_5$	109—109,5 (0,5)	84,5	1,4927	0,9402	91,3	90,70
II	$(CH_3)_2C_6H_5SiOSi(CH_3)_2CH_2NHC_6H_5$	123—125 (1)	—	1,5310	1,0047	97,18	96,47
III	$(C_2H_5)_3SiO\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2NHC_6H_5}{\overset{|}{\underset{|}{Si}}}}—O—Si(C_2H_5)_3$	145—150 (0,5)	71	1,4825	0,9514	123,4	123,43
IV	$(C_2H_5)_3Si—O—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2N(C_2H_5)_2}{\overset{|}{\underset{|}{Si}}}}—O—Si(C_2H_5)_3$	102—106 (1)	78,5	1,4410	0,8882	116,5	117,76
V	$(C_2H_5)_3Si—O—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2NC_4H_8O}{\overset{|}{\underset{|}{Si}}}}—O—Si(C_2H_5)_3$	129—131 (1)	74,6	1,4525	0,9425	116,3	117,43
VI	$(C_2H_5)_3Si—O—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2NHC_6H_4Cl}{\overset{|}{\underset{|}{Si}}}}—OSi(C_2H_5)_3$	151—153 (0,5)	48	1,4885	1,000	128,55	128,29
VII	$(CH_3)_2C_6H_5Si—O—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2NHC_6H_5}{\overset{|}{\underset{|}{Si}}}}—OSi(CH_3)_2C_6H_5$	187—195 (1)	—	1,5381	1,0534	134,18	134,98
VIII	$C_6H_5NHCH_2(CH_3)_2SiO—\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_2H_5}{\overset{|}{\underset{|}{Si}}}}—O—Si(CH_3)_2CH_2NHC_6H_5$	173—175 (0,5)	—	1,5218	1,023	133,1	132,8

1,1,2,2-Tetramethyl-1-phenyl-2-phenylaminomethyldisiloxane (II). Analogously, 2.8 g (0.018 M) of dimethylphenylsilanol and 4.0 g (0.019 M) phenylaminomethyldimethylethoxysilane yielded 2 g of a product boiling at 123 to 125° (1 mm) (see table). Found: C 64.41, 64.66; H 7.87, 7.95; Si 18.07, 17.87; N 4.37, 4.17%. $C_{17}H_{25}Si_2NO$. Calculated: C 64.70; H 7.98; Si 17.80; N 4.43%.

1,1,3,3-Tetramethyl-2,2-diethyl-1,3-di-(phenylaminomethyl)trisiloxane (VIII). Analogously, when 10.4 g (0.05 M) phenylaminomethyldimethylethoxysilane reacted with 3.0 g (0.025 M) diethylsilandiole, the product was 2.5 g of a substance boiling at 173-175° (0.5 mm) (see table). Found: C 59.35, 59.62; H 8.58, 8.58; Si 18.59, 18.33; N 6.52, 6.31%. $C_{22}H_{38}Si_3N_2O_2$. Calculated: C 59.13; H 8.50; Si 18.86; N 6.27%.

SUMMARY

1. The reaction of alkyl(aryl)aminomethylethoxysilanes with alkyl(aryl)hydroxysilanes was studied, and it was established that the introduction of a nitrogen atom into the organic group greatly enhances the reactivity in the α-position of the alkoxy group regarding exchange for the trialkyl(aryl)siloxy group.

2. Eight new compounds containing two and three silicon atoms per molecule were synthesized and characterized.

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ADDITION OF ALKOXYSILANEHYDRIDES TO UNSATURATED NITRILES AND HYDROGENATION OF THE ω-CYANOALKYLALKOXYSILANES OBTAINED

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The reaction of unsaturated nitriles with silicochloroform and alkylsilanechlorohydrides has been described in detail in the literature [1-5]. In the presence of platinum catalysts the $SiCl_3$ group of silicochloroform adds to acrylonitrile in the β-position [1-2]:

$$CH_2=CHCN + HSiCl_3 \rightarrow Cl_2SiCH_2CH_2CN.$$

Methyldichlorosilane reacts with acrylonitrile to form a mixture of α- and β-addition products [2]:

$$CH_2=CHCN + CH_3SiCl_2H \rightarrow CH_3-\underset{\underset{Si\,(CH_3)\,Cl_2}{|}}{CH}-CN + (CH_3)\,Cl_2SiCH_2CH_2CN.$$

In the case of unsaturated nitriles whose molecules contain the $-C\equiv N$ and $CH_2=CH-$ groups, one or more of the methylene groups is released, and the CH_3SiCl_2 group of the methyldichlorosilane occurs at the end of the molecule of the olefin [3]:

$$CH_2=CH\,(CH_2)_nCN + CH_3SiCl_2H \rightarrow CH_3Cl_2SiCH_2CH_2\,(CH_2)_nCN,$$

where $n \geq 1$.

At the same time, the problem of the addition of alkoxysilanehydrides to cyanoolefins has not been elucidated at all in the original literature. In a patent [6] the possibility is indicated of the addition of alkoxysilanehydrides to unsaturated nitriles in the presence of organophosphorus compounds as catalysts and at increased pressure.

The purpose of the present work was to investigate the possibility of the addition of alkoxysilanehydrides to unsaturated nitriles (allylcyanide, the β-cyanoethyl ether of allyl alcohol, and acrylonitrile) and to study the hydrogenation of the cyanoalkylethoxysilanes produced. As a result of the investigation which we carried out, we established that the addition proceeds according to the scheme

$$R'(RO)_2SiH + CH_2=CHCH_2X \rightarrow R'(RO)_2SiC_4H_4CH_2X,$$

where R' = $-CH_3$, $-OC_2H_5$, or $-OCH_3$; R = $-CH_3$ or $-C_2H_5$; X = $-OCH_2CH_2CN$ or $-CN$.

The reaction went at atmospheric pressure when a mixture of equimolar quantities of the reagents was boiled in the presence of Pt/C (20% Pt) or of a 0.1 N solution of H_2PtCl_6 in isopropyl alcohol. The yields of the addition products amounted to 40-50% based on the components used, and up to 85% on the basis of the unsaturated nitrile that reacted. When the reaction was carried out in sealed glass ampules at 150-180°, the yields of the products could be increased, and the reaction time considerably shortened. In all cases, the main reaction was accompanied by disproportionation of the alkoxy radicals of the starting alkoxysilanehydrides:

$$2\,(C_2H_5O)_3SiH \rightarrow (C_2H_5O)_4Si + [(C_2H_5O)_2SiH_2],$$

and the dihydride produced underwent further disproportionation.

TABLE 1. Properties of Organosilicon Nitriles and Dinitriles

No.	Formula of compound	B. p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.	Found %	Calc., %
I	$NCCH_2CH_2CH_2SiCl_3$	111—112 (12)	—	—	—	—	Cl 52,15	Cl 52,55
II	$NCCH_2CH_2OCH_2CH_2CH_2SiCl_3$	147—148 (8)	—	—	—	—	Cl 43,19	Cl 43,16
III	$NCCH_2CH_2CH_2Si(OC_2H_5)_3$	117—119 (6)	1,4161	0,9671	60,04	60,22	C 52,06; 51,93 H 9,26; 9,18 Si 12,45; 12,47	C 51,91 H 9,14 Si 12,14
IV	$NCCH_2CH_2OCH_2CH_2CH_2Si(OC_2H_5)_3$	142 (3)	1,4270	0,9932	71,19	71,25	C 52,35; 52,19 H 9,17; 9,23 Si 10,35; 10,41	C 52,32 H 9,15 Si 10,19
V	$NCCH_2C_2H_4Si(OC_2H_5)_2CH_3$	99,5—101 (5)	1,4225	0,9360	54,70	55,03	Si 14,35; 14,18 C 53,38; 53,34 H 9,45; 9,20	C 53,68 Si 13,95 H 9,51
VI	$NCCH_2CH_2OCH_2C_2H_4Si(OC_2H_5)_2CH_3$	133—136 (2)	1,4312	0,9656	66,06	65,86	Si 11,41	Si 11,44
VII	$NCCH_2CH_2OCH_2CH_2CH_2Si(OCH_3)_3$	130—132 (2)	1,4290	1,0534	57,10	57,36	Si 12,21	Si 12,04
VIII	$[NCCH_2CH_2Si(OC_2H_5)_2]_2O$	204,5—205,5 (7)	1,4270	1,0419	88,84	88,76	N 8,12; 7,89	N 7,77
IX	$[NCCH_2CH_2CH_2Si(OC_2H_5)_2]_2O$	186—189 (1)	1,4312	1,0281	97,93	98,02	C 49,48; 49,28 H 8,47; 8,43 Si 14,51; 14,27	C 49,44 H 8,32 Si 14,45
X	$[NCCH_2CH_2OCH_2CH_2CH_2Si(OC_2H_5)_2]_2O$	256—257 (4)	1,4411	1,0542	121,40	120,08	Si 11,98; 12,00	Si 11,58

A study of the IR absorption spectra of the ω-cyanoalkyltrichlorosilanes* that we obtained showed the absence of frequencies characteristic of the $-CH_3$ group. On the basis of this fact, we ascribed the following structure to the nitriles that were obtained: $Cl_3SiCH_2CH_2CH_2CN$ and $Cl_3SiCH_2CH_2CH_2OCH_2CH_2CN$.

The ω-cyanoalkyltrialkoxysilanes which were prepared by the addition of trialkoxysilanehydrides to unsaturated nitriles, and those which were obtained by the addition of $HSiCl_3$ to unsaturated nitriles with subsequent esterification of the ω-cyanoalkyltrichlorosilanes with alcohols had identical properties. This permits the conclusion that the addition of $(RO)_3SiH$ to the unsaturated nitriles proceeds in a similar manner to the addition of Cl_3SiH, i.e., the trialkyloxysilyl group is located at the end of the molecule. When $CH_3(OC_2H_5)_2SiH$ reacts with unsaturated nitriles, it is possible that a mixture of isomeric products of addition at the double bond is formed, as is indicated by the wide boiling ranges of the products obtained. On the basis of the data in [7], it also might be expected that products of the reaction of the silanehydrides with the unsaturated nitriles at the site of the triple bond of the $-C\equiv N$ group would be formed. In our study of the IR spectra of the products of addition of $HSiCH_3(OC_2H_5)_2$ to $CH_2 = CHCH_2CN$ and $CH_2 = CHCH_2OCH_2CH_2CN$ however, we did not observe frequencies characteristic of the $CH_2 = CH-$ and $=N-N$ groups, which indicates addition only at the double bond.

We were not successful in adding $(C_2H_5O)_3SiH$ to acrylonitrile either at atmospheric pressure or at increased pressures (in glass ampules at 150-180°) in the presence of the catalysts Pt/C, H_2PtCl_6, $(CH_3)_2NC(=O)H$, $(C_4H_9)_3N$, $SnCl_4$, $(C_6H_5COO)_2O - SnCl_4$ mixture, etc. Under these conditions polymerization of acrylonitrile and disproportionation of the triethoxysilane occurred, or the starting materials were recovered unchanged. Hydrogenation of the ω-cyanoalkyltriethoxysilanes obtained to the corresponding primary amines was carried out in the presence of skeletal Co or Ni catalysts under pressure by the method described by us earlier [8-10]. In the process of studying the hydrogenation reaction, it was established that the nature of the catalyst and the structure of the nitrile, as would be expected, have considerable effect on the yield of primary amine. In all cases in the presence of Co catalyst the reaction proceeded more selectively than with nickel: the yield of amine was higher, and the residue less. The yield of amine when a γ-cyanoalkyltrialkoxysilane was hydrogenated was higher than when β-cyanoethyltriethoxysilane was reduced. In the present work we also showed the possibility of hydrogenating α,ω-(dicyanoalkyl)tetraethoxydisiloxanes to the corresponding primary α,ω-diamines. The α,ω-dinitriles mentioned were obtained as byproducts in the esterification of ω-cyanoalkyltrichlorosilanes.

EXPERIMENTAL

The properties of the nitriles and dinitriles obtained are given in Table 1; the conditions and results of their hydrogenation in Table 2, and the properties of the amines in Table 3.

The alkoxysilanehydrides were prepared by the action of absolute alcohols on $HSiCl_3$ or $(CH_3)SiHCl_2$ at 0° in the presence of pyridine as an acceptor of hydrogen chloride; they had the following properties: $(C_2H_5O)_3SiH$, b.p. 135°, $n^{20}D$ 1.3771, d^{20}_4 0.8965; $(C_2H_5O)_2SiCH_3H$, b.p. 101°, $n^{20}D$ 1.3769.

Synthesis of $Cl_3SiCH_2CH_2CH_2CN$ (I). To 26.8 g (0.4 M) of allyl cyanide at 110° was added 4 drops of 0.1 N solution of H_2PtCl_6 in isopropyl alcohol, and then 43 g (0.4 M) of silicochloroform was added over the course of 4 hr. After the temperature of the mixture reached 155°, another 8 g of $HSiCl_3$ was added, and the mixture was boiled for 3 hr. By fractional distillation 58.5 g of crude (I) was isolated with b.p. 110-112° (12 mm); yield 72.2% based on the unsaturated nitrile used.

Synthesis of $Cl_3SiCH_2CH_2CH_2OCH_2CH_2CN$ (II). To 122 g (1.1 M) of β-cyanoethyl ether of allyl alcohol at 100° was added 4 drops of 0.1 N H_2PtCl_6 solution in isopropyl alcohol, and then 147.7 g (1.1 M) of $HSiCl_3$ was added over the course of 5 hr. After addition of an excess (28 g) of $HSiCl_3$, the mixture boiled at 98°. By fractional distillation 154 g of crude (II) was isolated with b.p. 145-150° (8 mm); yield 57.3% based on the unsaturated nitrile used.

Synthesis of $(H_5C_2O)_3SiCH_2CH_2CH_2CN$ (III). From allyl cyanide and triethoxysilane. To a mixture of 50 g (0.3 M) of triethoxysilane, 2 drops of 0.1 N solution of H_2PtCl_6 in isopropyl alcohol, and 10 g of allyl cyanide, after boiling for 2 hr, was added 20 g of allyl cyanide (0.3 M) and boiling was continued until the boiling point reached 149° and did not change for 2 hr. As a result of fractionation of the reaction products, we obtained 7 g of the starting nitrile, 6 g of tetraethoxysilane with b.p. 164.5°-168°, and $n^{20}D$ 1.3840, and 33.5 g of γ-cyanopropyltriethoxysilane. The yield of the last-named compound was 48% based on the allyl cyanide used, and 65.5% based on the allyl cyanide that reacted. When a mixture of 23.5 g of $(C_2H_5O)_3SiH$ and 9.5 g of $CH_2 = CHCH_2CN$ was boiled with 0.05-0.3 g of platinized carbon (Pt 20%), the addition reaction did not go and the allyl cyanide was recovered from the reaction.

*In the region of the valence vibrations (2800-3000 cm^{-1}; LiF prism) and deformation vibrations (1300-1500 cm^{-1}; NaCl prism).

TABLE 2. Catalytic Hydrogenation of Cyanoalkylsilanes in the Presence of Skeletal Catalysts

Starting nitrile	Catalyst	Hydrogenation conditions			Comp. of reaction mix., %		Yield of amine based on nitrile, %
		temp., °C	Initial H_2 pressure, in atm.	nitrile, ethanol, (vol.)	amine	residue	
$(C_2H_5O)_3SiCH_2CH_2CN$	Ni	85	110	1:1	39,6	60,4	33,0
the same	Co	80	120	1:1	76	24	61,0
$(C_2H_5O)_3SiCH_2CH_2CH_2CN$	Co	85	100	1:1	81	19	73,0
$(C_2H_5O)_3SiCH_2CH_2CH_2OCH_2CH_2CN$	Ni	85	100	1:1	42	58	30,0
the same	Co	80	105	1:1	70	30	53,0
$[NCCH_2CH_2Si(OC_2H_5)_2]_2O$	Co	80	100	1:1	61	39	46,0
$(C_2H_5O)_3SiCH_2CH_2CN$	Co*	85	100	1:1	65	35	50,0

*Co boride.

TABLE 3. Properties of Organosilicon Amines and Diamines

Formula of compound	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR	
				found	calc.
$NH_2CH_2CH_2CH_2CH_2Si(OC_2H_5)_3$	105—107,5 (6)	1,4243	0,9408	63,86	63,79
$NH_2CH_2CH_2CH_2OCH_2CH_2CH_2Si(OC_2H_5)_3$	112—115 (1)	1,431.	0,9648	75,28	74,84
$NH_2CH_2CH_2CH_2Si(OC_2H_5)_2]_2O$	174—176 (6)	1,438[illegible]	1,0056	96,32	95,94

From γ-cyanopropyltrichlorosilane and ethanol. To a mixture of 36.8 g (0.08 M) of absolute ethanol and 63.2 g of pyridine (0.08 M) in 200 ml of absolute ether was added, over the course of 2 hr with stirring, 40 g (0.2 M) of $Cl_3SiCH_2CH_2CH_2CN$, and the mixture was stirred for another 6 hr. The next day, after the pyridine salt formed had been filtered off with suction and the solvent had been distilled off, (III) was obtained with b.p. 108° (4 mm); $n^{20}D$ 1.4168; d^{20}_4 0.9673; found: MR 60.11; calculated MR 60.22, and also the disiloxane $[NCCH_2CH_2CH_2Si(OC_2H_5)_2]_2O$ (IX) (see Table 1).

Synthesis of $(C_2H_5O)_3SiCH_2CH_2CH_2OCH_2CH_2CN$ (IV). From β-cyanoethyl ether of allyl alcohol and triethoxysilane. When a mixture of 25 g (0.225 M) of β-cyanoethyl ether of allyl alcohol, 37 g (0.225 M) of triethoxysilane, and 0.05 g of platinized carbon (20% Pt) was boiled for 11 hr, the boiling point rose from 144 to 165°. Then, after the $(C_2H_5O)_3SiH$ and $(OC_2H_5)_4Si$ had been distilled off, 12 g of the starting nitrile with b.p. 78-86° (6 mm) and $n^{20}D$ 1.4315, and 24 g of crude (IV) with b.p. 152-170° (6-8 mm) and $n^{20}D$ 1.4268 were isolated. Upon repeated distillation the b.p. of (IV) was 142° (3 mm); the yield was 38% based on the reagents used, and 81% based on the nitrile reacted.

By the same method we prepared $NCCH_2CH_2CH_2Si(OC_2H_5)_2CH_3$ (V) (see Table 1), b.p. 120° (16 mm) to 130° (17 mm), $n^{20}D$ 1.4209, d^{20}_4 1.4260, yield based on reagents used 45%; and $NCCH_2CH_2OCH_2CH_2CH_2Si(OC_2H_5)_2CH_3$ (VI) (see Table 1), b.p. 117-125° (1 mm), $n^{20}D$ 1.4300, d^{20}_4 1.4314, yield based on reagents 54%. Upon repeated distillation the materials also boiled over wide ranges. The middle fractions were taken for analysis.

From γ-(β-cyanoethoxy)propyltrichlorosilane and ethanol. To a mixture of 29.44 g (0.64 M) of absolute ethanol and 50.5 g (0.64 M) of pyridine in 250 ml of absolute ether was added, over the course of 2 hr, with stirring, 40 g (0.16 M) of $Cl_3SiCH_2CH_2CH_2OCH_2CH_2CN$ and stirring was continued for another 6 hr at 20°. After the usual treatment, 9 g of crude (IV) was isolated with b.p. 156-159° (5 mm), contaminated with chlorine-containing compounds. By repeated treatment of this material with alcohol and pyridine an analytically pure product was obtained with b.p. 125.5-125.8° (1 mm), $n^{20}D$ 1.4269, d^{20}_4 0.9928; MR found 71.20; MR calculated 71.25. Furthermore, we obtained from the experiment 9 g of a fraction with b.p. 260-261° (5 mm) which was the disiloxane $[NCCH_2CH_2OCH_2CH_2CH_2Si(OC_2H_5)_2]_2O$ (X) (Table 1).

Synthesis of $(C_2H_5O)_3SiCH_2CH_2CN$. By a method similar to that used in the preceding experiments, we reacted $Cl_3SiCH_2CH_2CN$ (188 g), C_2H_5OH (184 g), and pyridine (316 g) in solution in 1.2 liters of heptane. We obtained 130 g of β-cyanoethyltriethoxysilane (60% based on the $Cl_2SiCH_2CH_2CN$ used) with b.p. 123-126° (15 mm), $n^{20}D$ 1.4136. The compound obtained contained practically no hydrolyzable chlorine. Furthermore, in this experiment we obtained 20 g of the siloxane $[NCCH_2CH_2Si(OC_2H_5)_2]_2$ (VIII) with b.p. 204.0-205.5° (7 mm). In a similar manner, we obtained $NCCH_2CH_2OCH_2CH_2CH_2Si(OCH_3)_3$ (VII).

Hydrogenation of ω-cyanoalkylalkoxysilanes. Hydrogenation of the nitriles that had been prepared was carried out in a rotating autoclave. The catalyst and the conditions of hydrogenation are shown in Table 2. The nickel catalyst was prepared by exhaustive leaching of a Ni–Al alloy (50:50) by boiling in 10% sodium hydroxide solution. The Co catalyst was prepared by a method previously described [11]. The amount of the catalyst used in the experiments was 20-25% of the weight of the nitrile taken for the reaction. To avoid hydrolysis of the ω-cyanoalkylalkoxysilanes, the reaction was carried out in absolute alcohol and the hydrogen supplied to the autoclave was dried over granulated potassium hydroxide. The catalysate was distilled first at atmospheric pressure (to remove the alcohol), and then at decreased pressure (to remove the amine fraction). The purity of the amine fraction was determined by the acidimetric method. From Table 2 it can be seen that when $(C_2H_5O)_3SiCH_2CH_2CN$ and $(C_2H_5O)_3SiCH_2CH_2CH_2OCH_2CH_2CN$ were hydrogenated, the yield of the corresponding ω-aminoalkyltriethoxysilane obtained with the Co catalyst was almost twice as high as with the Ni catalyst under similar conditions. Under identical conditions of hydrogenation the corresponding ω-aminoalkyltriethoxysilanes were produced in higher yields from γ-cyanopropyltriethoxysilane than from β-cyanoethyltriethoxysilane.

Experiments on repeated hydrogenation showed that on the same portion of skeletal cobalt catalyst it was possible to carry out numerous hydrogenations (up to 20 times) without a decrease in yield of the amine fraction. In the presence of contaminating halogen-containing compounds in the starting ω-cyanoalkyltrialkoxysilanes, the length of service of the catalyst and the yield of the amine fraction were considerably diminished. Hydrogenation of ω-cyanoalkyltrialkoxysilanes also could be carried out in the presence of Co/Al_2O_3 or Co boride catalyst. The latter was prepared by a previously described method [12]. In the experiment with the boride catalyst, the yield of γ-aminopropyltriethoxysilane was somewhat lower than with the skeletal cobalt catalyst. Furthermore, we determined that the use of ammonia as the medium for the hydrogenation of ω-cyanoalkyltriethoxysilanes was possible only after it was carefully dried.

SUMMARY

1. The alkoxysilanehydrides add to $CH_2 = CHCH_2CN$ and $CH_2 = CHCH_2OCH_2CH_2CN$ at the double bond in the presence of platinum catalysts at atmospheric pressure.

2. The order of addition (according to Farmer's rule) of triethoxysilane and trichlorosilane to $CH_2 = CHCH_2CN$ and $CH_2 = CHCH_2OCH_2CH_2CN$ in the presence of platinum catalysts has been demonstrated.

3. The conditions for the hydrogenation of ω-cyanoalkylalkoxysilanes on skeletal nickel and cobalt catalysts to the corresponding ω-aminoalkylalkoxysilanes have been worked out.

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ESTERS OF β-KETOPHOSPHONIC ACIDS.

COMMUNICATION 8. REACTION OF 2,6-DIBROMOCYCLOHEXANONE WITH TRIETHYL PHOSPHITE

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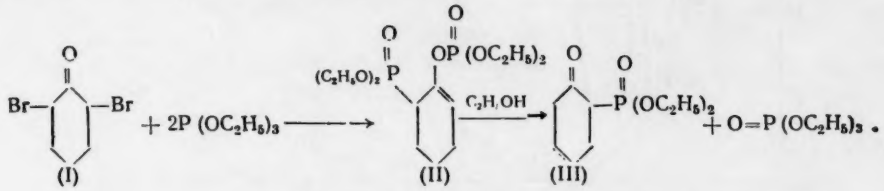
The synthesis of esters of cyclohexanone-2-phosphonic-1 acid encounters considerable difficulties, since the usual routes of synthesis of esters of phosphonic acids – the rearrangement reaction of A. E. Arbuzov and the Michaelis-Becker reaction – lead to other products [1]. In a short communication [2] we presented a route for the synthesis of an ester of cyclohexanone-2-phosphonic-1 acid starting from 2,6-dibromocyclohexanone through the mixed phosphoric ester of the enol form of cyclohexanone-2-phosphonic acid:



In that communication it was indicated that the reaction between triethyl phosphite and 2,6-dibromocyclohexanone does not go smoothly, but is accompanied by the formation of a number of byproducts, and depends to a great extent on the reaction conditions. In addition to the main reaction product (II), low-boiling fractions are formed and also a product which is difficult to separate from the ester (II) and contains a larger percentage of phosphorus.

In the present communication we present the results of a more detailed investigation of the products obtained by the action of triethyl phosphite on 2,6-dibromocyclohexanone. The reaction between (I) and triethyl phosphite proceeds in a complex manner. We have not determined all the directions of reaction with certainty, but the main directions of interaction of triethyl phosphite with 2,6-dibromocyclohexanone have been established. One of the causes of the complex course of this reaction may be the different reactivity of the conformational isomers of 2,6-dibromocyclohexanone. Therefore, the first series of experiments was carried out with trans-2,6-dibromocyclohexanone. It should be noted, however, that under the conditions of the experiment partial isomerization of the trans-isomer to the cis-isomer could occur. Such an isomerization has been observed in the case of cis- and trans-2,6-dichlorocyclohexanone [3].*

The main product of the reaction between trans-(ae)-2,6-dibromocyclohexanone and triethyl phosphite was the diethylphosphoric ester of the enol form of the ester of cyclohexan-2-onephosphonic-1 acid (II) (about 50%); its structure was demonstrated both by analytical data** and by preparation from it of the ester of cyclohexanone-2-phosphonic-1-acid (III) by a transesterification reaction with ethyl alcohol [4]. The constants of the ester (III) coincided with the constants of the ester (III) obtained by saponification of the ester of 1-ethoxycyclohexene-1-phosphonic-2 acid [2]. The dinitrophenylhydrazone of the ester (III) melted at 109-109.5°.

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* We observed the transition of trans-2,6-dibromocyclohexanone with m.p. 36° to the cis-isomer on recrystallization and prolonged standing in a desiccator.

** It should be pointed out that the phosphorus content of fraction (II) as a rule exceeded the calculated amount by 0.3-0.7%.

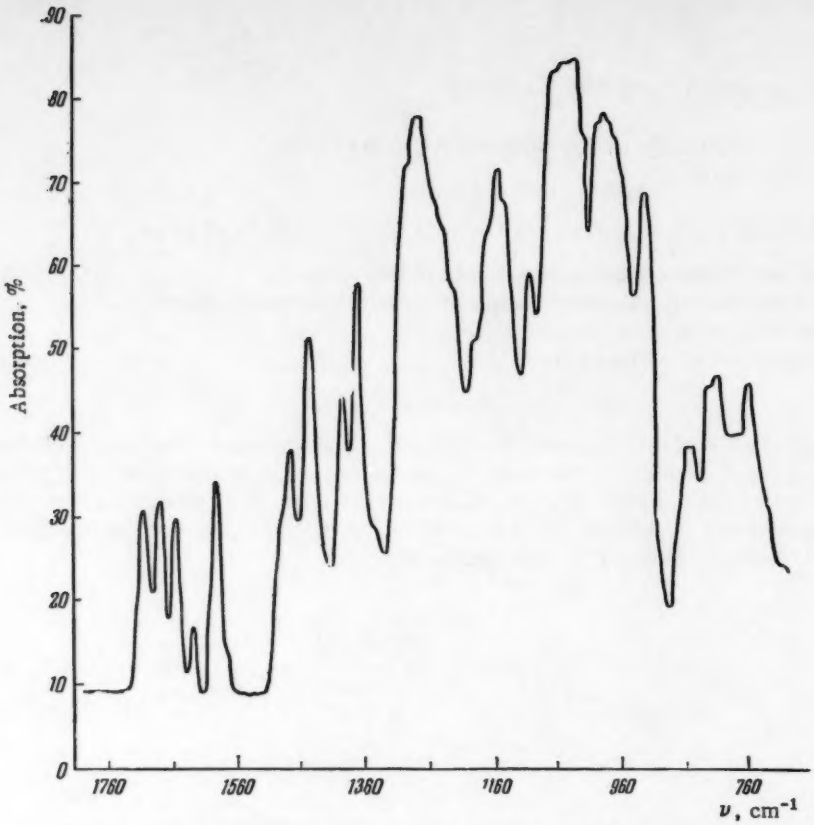


Fig. 1. IR absorption spectrum of fraction with b.p. 104-107° (2.5 mm).

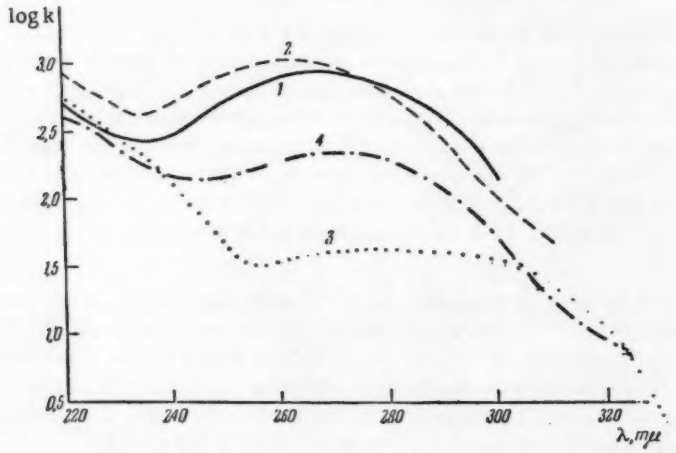


Fig. 2. UV absorption spectra of solutions in methanol: 1) product with b.p. 120-122° (4 mm); chromatographic fractions of product with b.p. 120-122° (4 mm); 2) 111-112° (2 mm); 3) 109-110° (1.5 mm); 4) 138-141° (3.5 mm).

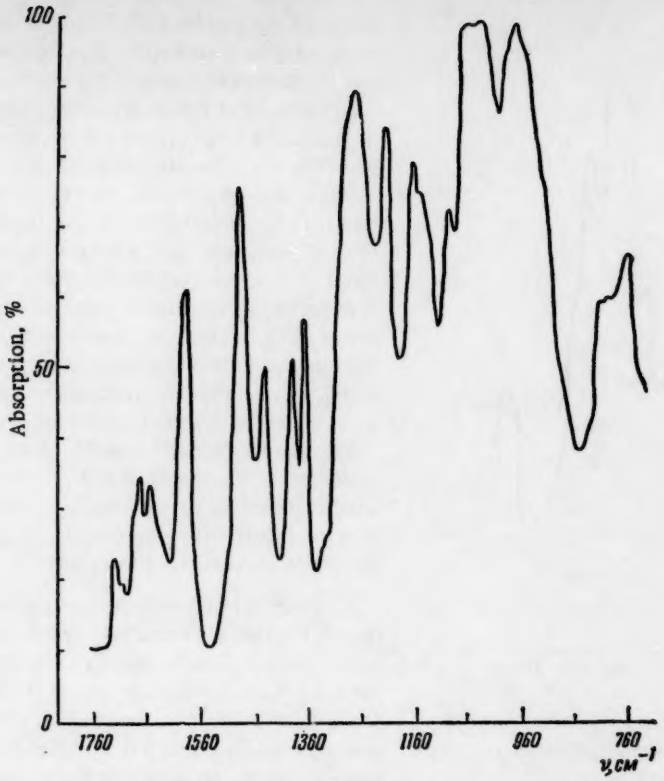


Fig. 3. IR absorption spectrum of chromatographic fraction with b.p. 111-112° (2 mm).

The Raman spectra [4], the IR spectra [2], and the UV spectra [4] of the two preparations proved to be identical. An investigation was made of the low-boiling fractions by fractional distillation and study of the spectra of the fractions obtained. Fractional distillation of the lowest fractions on a column of 8 theoretical plates permitted separation of diethylphosphorous acid and triethyl phosphate. The fractions boiling above triethyl phosphate, at 100-160° (2.5 mm) on the column of 8 theoretical plates decomposed. These fractions, therefore, after distillation from an Arbuzov flask, were subjected to spectral analysis. A fraction was separated with b.p. 104-107° (2.5 mm), $n^{20}D$ 1.4703, d^{20}_0 1.1455 (about 25%), which, with respect to its phosphorus analysis, closely approached the diethyl ester of cyclohexanone-2-phosphonic acid.* A study of the IR and Raman spectra of this fraction showed, however, that it was a complex mixture of products of similar composition.

The Raman spectrum of the fraction with b.p. 104-107° (2.5 mm) had the following frequencies (cm^{-1}):

240 (0), 298 (1), 330 (0), 494 (0), 556 (0), 614 (0), 657 (1), 744 (2b),** 793 (0), 815 (2), 836 (2), 848 (1), 917 (0), 948 (1), 980 (1), 1003 (2b),** 1025 (3), 1047 (1), 1077 (1), 1101 (3), 1156 (2), 1174 (1), 1243 (4), 1267 (1), 1293 (1), 1305 (1), 1343 (1), 1371 (1), 1394 (2), 1435 (3), 1450 (3), 1487 (1), 1535 (2), 1573 (2), 1595 (8), 1634 (4), 1659 (1), 1684 (2), 2730 (0), 2840 (2), 2871 (2), 2899 (3), 2936 (6), 2978 (3), 3053 (3), 3068 (3).

The IR spectrum of the fraction with b.p. 104-107° (2.5 mm) is given in Fig. 1; in it there are absorption bands at 1591, 1629, 1655, 1679, and 1708 cm^{-1}. The frequencies 1679 cm^{-1} in the IR spectrum and 1684 and 3068 cm^{-1} in the Raman spectrum may indicate the presence of the mixed diethylcyclohexen-1-yl-1 ester of phosphoric acid [1]*** or of diethylbromo-6-cyclohexen-1-yl phosphoric ester.**** The frequency 1708 cm^{-1} in the IR spectrum

*Phosphorus content 1.2% less than calculated for (III).

**b = broad line.

***The mixed ester could be produced as a result of contamination of the 2,6-dibromocyclohexanone with monobromocyclohexanone.

****For details see the following communication.

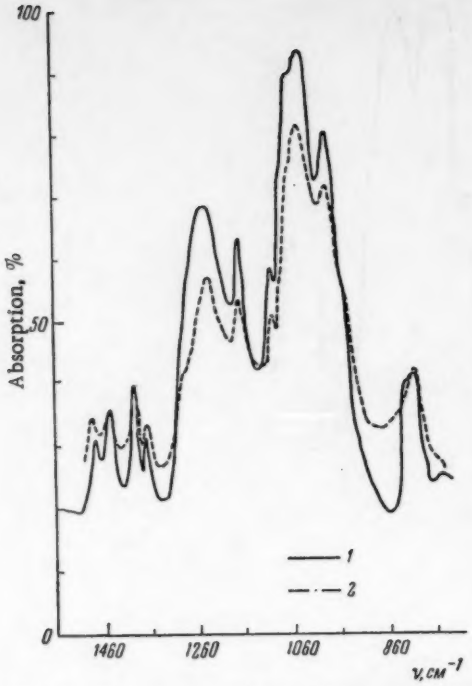


Fig. 4. IR absorption spectra: 1) chromatographic fraction b.p. 138-141° (3.5 mm); 2) tetraethyl ester of hypophosphoric acid.

indicates the presence of the diethyl ester of cyclohexanone-2-phosphonic-1 acid (III). The infrared frequency 1629 cm^{-1} and the Raman frequency 1633 cm^{-1} indicate the presence of the enol form of the diethyl ester of cyclohexanone-2-phosphonic acid. The frequencies in the Raman spectrum 1535, 1573, and 1595 cm^{-1} may indicate the presence of compounds with conjugated double bonds. As will be shown further, in the fraction with b.p. 104-107° (2.5 mm) the mixed diethyl phenyl ester of phosphoric acid was present, as well as unsaturated esters of phosphoric acid. The formation of these products was demonstrated with greater conclusiveness in the experiment between cis-2,6-dibromocyclohexanone (ee) and triethyl phosphite. The cis-2,6-dibromocyclohexanone (ee) [5] used for the reaction melted after recrystallization from ether at 104-106°; its IR spectrum had the frequencies of the C = O group at 1750 (s) and 1730 cm^{-1} (m) [6]. From the products of the reaction of the dibromide of m.p. 104-106° with two moles of triethyl phosphite we isolated from the lower fractions, after fractional distillation, diethylphosphorous acid and triethyl phosphate, as confirmed by their constants and IR spectra.

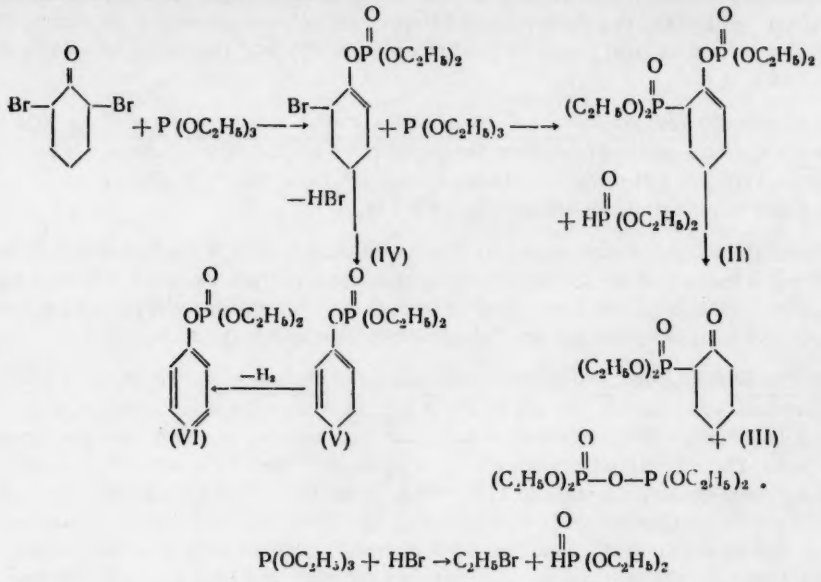
From the high-boiling fractions we isolated, by distillation, a fraction with b.p. 120-122° (4 mm), $n^{20}D$ 1.4630, d^{20}_0 1.1225, which corresponded in its analysis* and constants to the diethyl ester of cyclohexanone-2-phosphonic-1 acid. With ferric chloride the fraction gave an intense lilac color; its IR spectrum coincided with that of the diethyl ester of cyclohexanone-2-phosphonic acid with the exception of weak absorption bands at 1655 and 1591 cm^{-1} and a shoulder in the direction of the higher frequencies on the absorption band of the P = O group which were absent from the spectrum of the ester (III). The Raman spectrum of this fraction confirmed the data of the IR spectrum [frequencies for C = O at 1713 (1) and C = C at 1634 (6) cm^{-1}]. The fraction contained contaminating unsaturated compounds [frequencies at 1573 (9), 1595 (4), 3044 (4), and 3070 (2) cm^{-1}]. The UV spectrum had an absorption maximum at 267.5 mμ (log k 2.9) and absorption in the region of 220 mμ (log k 2.7) (Fig. 2, Curve 1).

For a more detailed investigation of the fraction with b.p. 120-122° (4 mm), it was subjected to chromatography on silica gel and elution with petroleum ether + ether and ether + ethyl alcohol. The first fraction from the chromatography had the b.p. 111-112° (2 mm), $n^{20}D$ 1.4720; its IR spectrum (Fig. 3) was very similar to that of diethyl phenyl phosphate [7] (frequencies 1591, 1489, 1270, 1211 cm^{-1}, etc.). The fraction was contaminated with small amounts of phosphonocyclohexanone (III) (frequencies 1708 C = O and 1629 C = C), and a product with conjugated double bonds (frequency 1655 cm^{-1})**; its UV spectrum (Fig. 2, Curve 2) had an absorption maximum at 262.5 mμ (log k 3.04) and 220 mμ (log k 2.94), which indicated the presence of conjugated bonds. The product extracted with 75% ether + 25% petroleum ether proved to be the diethyl ester of cyclohexanone-2-phosphonic-1 acid [b.p. 109-110° (1.5 mm), $n^{20}D$ 1.4653, d^{20}_0 1.1255]; it gave a bright violet color with $FeCl_3$; its identity with (III) was also shown by the IR spectrum and the UV spectrum (Fig. 2, Curve 3). From the fraction eluted by ether + 10% alcohol we isolated a product with b.p. 138-141° (3.5 mm), $n^{20}D$ 1.4300, containing 16.78% P. The UV spectrum of the fraction is shown in Fig. 2, Curve 4. The IR spectrum indicates the presence in the fraction of the tetraethyl ester of hypophosphoric acid, as can be seen from Fig. 4, where the spectra of the latter and of the fraction with b.p. 138-141° (3.5 mm) are given.

*The amount of phosphorus found exceeded the calculated value by 1g .

**Comparison of the IR spectra of this fraction and the fraction with b.p. 104-107° (2.5 mm) (Fig. 1) of the experiment with trans-2,6-dibromocyclohexanone showed the presence of common absorption bands.

The data obtained permit us to give the following diagram for the complex course of the reaction when triethyl phosphite acts on 2,6-dibromocyclohexanone:



$$P(OC_2H_5)_3 + HBr \rightarrow C_2H_5Br + HP(OC_2H_5)_2$$

The unsaturated bromocyclohexenyl ester of phosphoric acid (IV) can react with a second molecule of triethyl phosphite to give (II) or to split out a molecule of hydrogen bromide with the formation of diethyl cyclohexadienyl ester of phosphoric acid (V). The latter is dehydrogenated to the diethyl phenyl ester of phosphoric acid (VI). The ease of aromatization of cyclohexadiene derivatives has been mentioned more than once in the literature [8]. The hydrogen bromide split out with triethyl phosphite gives diethylphosphorous acid which, reacting with ester (II), yields the ester of cyclohexanonephosphonic acid and tetraethyl hypophosphate. The hypophosphate ester was not isolated in the pure form, although fractions close to it in their constants were obtained on chromatographing. Contamination with the hypophosphate ester may explain the high phosphorus content of the ester of cyclohexanonephosphonic acid. The possibility of forming the ester of cyclohexanonephosphonic acid by the action of diethylphosphorous acid on ester (II) was confirmed by an experiment on the action on ester (II) of diethylphosphorous acid with the formation of ester (III). The IR and UV spectra of the product of the action of diethylphosphorous acid on ester (II) and of the transesterification of (II) with ethyl alcohol coincide completely. The route described for the preparation of the ester of cyclohexanonephosphonic acid is not unique. As has been shown by experiment, when ester (II) is heated to a high temperature it splits out diethylphosphorous acid which, according to the diagram given above, yields with ester (II) the ester of cyclohexanonephosphonic acid (III).

EXPERIMENTAL

The UV spectra were determined in an SF-4 quartz spectrophotometer. The IR spectra were determined for a capillary film of liquid in a Hilger H-800 spectrograph. The Raman spectra were determined in an ISP-51 spectrograph from the 4358 A excited blue line of a mercury lamp.

Preparation of 2,4-dinitrophenylhydrazone of the diethyl ester of cyclohexanone-2-phosphonic-1 acid. The experiment was carried out under the conditions described previously [1]. The diethyl ester of cyclohexanone-2-phosphonic-1 acid with b.p. 111-113° (1 mm) [2] gave the 2,4-dinitrophenylhydrazone upon prolonged standing. After repeated recrystallization from ethyl alcohol the m.p. was 109-109.5°. Found: P 7.26, 7.72%. $C_{16}H_{23}O_7PN_4$. Calculated: P 7.47%.

Action of triethyl phosphite on 2,6-dibromocyclohexanone of trans-structure. A fraction from one of the experiments described earlier [4] with b.p. 48-100° (2.5 mm) was distilled on a column of 8 theoretical plates. Two fractions were obtained: I) b.p. 47-49° (2.5 mm, $n^{20}D$ 1.4100, d^{20}_0 1.0642. Fraction I gave a dark lilac color with 3,5-dinitrobenzoic acid; it reacted with metallic sodium. II) Triethyl phosphate with b.p. 67.5-69.5° (3 mm), $n^{20}D$ 1.4122, d^{20}_0 1.0578. Fraction II did not give a color with 3,5-dinitrobenzoic acid nor react with metallic sodium.

Fractional distillation of the fraction with b.p. 100-160° (2.5 mm) was carried out in an Arbuzov flask. A fraction was obtained with b.p. 104-107° (4.5 mm), $n^{20}D$ 1.4703, d^{20}_0 1.1455 (11 g). Found: P 12.10, 11.95%. $C_{10}H_{19}O_4P$. Calculated: P 13.24%. With $FeCl_3$ in CH_3OH a weak, disappearing color was observed. A second distillation of the ester with b.p. 172.5-173° (2.5 mm) [4] yielded a product with b.p. 174-175° (3 mm); $n^{20}D$ 1.4673; d^{20}_0 1.2111. Found: P 17.53, 17.44%.

Action of diethylphosphorous acid on the diethylphosphoric ester of the enol form of the ester of cyclohexanone-2-phosphonic-1 acid (II). To a solution of sodium diethylphosphite in diethylphosphorous acid prepared from 5 g of diethylphosphorous acid and 0.2 g of metallic sodium was added 5.7 g of ester (II) with b.p. 174-175° (3 mm). The mixture was heated on a water bath in an Arbuzov flask for 7 hr.

Upon distillation the following were obtained: diethylphosphorous acid, a fraction with b.p. 53-57° (2.5-3 mm) triethyl phosphate, and a fraction of the diethyl ester of cyclohexanone-2-phosphonic-1 acid with b.p. 106-109° (3 mm), d^{20}_0 1.1063, $n^{20}D$ 1.4605, 1 g. The latter gave an intense lilac color with $FeCl_3$ in methanol. The reaction did not go to completion and a thick residue that did not distill remained in the flask.

Action of triethyl phosphite on 2,6-dibromocyclohexanone of cis-structure. To 38.6 g of triethyl phosphite placed in an Arbuzov flask was added in portions 29.8 g of 2,6-dibromocyclohexanone with b.p. 98-100° [5]. During this process partial solution of the dibromide took place. Complete solution occurred when the reaction mixture was heated on a water bath. The mixture was heated for 1.5 hr at 90-100°, then for 3 hr more on an oil bath. The temperature of the bath was gradually brought to 180°. Upon distillation of the mixture the following were obtained: 1) ethyl bromide, 21.6 g (theoretical 25 g); 2) a fraction with b.p. 38-62° (4 mm), 5 g; the latter gave an intense lilac color with 3,5-dinitrobenzoic acid, characteristic of diethylphosphorous acid; 3) a fraction with b.p. 66-69° (4 mm), 11.7 g, $n^{20}D$ 1.4075, d^{20}_0 1.0653 – triethyl phosphate (no color was obtained with 3,5-dinitrobenzoic acid); 4) a fraction with b.p. 120-122° (4 mm), 7 g, $n^{20}D$ 1.4630, d^{20}_0 1.1225, Found MR 57.47. Found: P 14.24, 14.08%. $C_{10}H_{19}O_4P$. Calculated: P 13.14%; with $FeCl_3$ in methyl alcohol solution it gave an intense lilac color.

The fraction with b.p. 120-122° (4 mm) was chromatographed on silica gel. For 4.2 g of material, 270 g of ASK brand silica gel with an activity of 6.5 units was used. Petroleum ether, diethyl ether, and methanol were employed as eluants.

The following fractions were obtained: I) b.p. 111-112° (2 mm),* $n^{20}D$ 1.4720, eluted with petroleum ether – diethyl ether mixture (1:1); II) b.p. 109-110° (1.5 mm),* $n^{20}D$ 1.4653, d^{20}_0 1.1255, 2 g eluted with a petroleum ether – diethyl ether mixture (1:3), with $FeCl_3$ in alcohol solution gave an intense lilac color; III) b.p. 138-141° (2.5 mm),* $n^{20}D$ 1.4300, 0.5 g, eluted with diethyl ether – methanol mixture (9:1); found: P 16.78%, gave no color with $FeCl_3$.

SUMMARY

1. The reaction of triethyl phosphite with 2,6-dibromocyclohexanone follows a complex course. In addition to the expected diethylphosphoric ester of the enol form of the ester of cyclohexanone-2-phosphonic-1 acid, by-products are formed which are produced by conversions of the latter compound (diethyl ester of cyclohexanone-2-phosphonic-1 acid and tetraethyl ester of hypophosphoric acid), and also an intermediate product, diethyl bromo-6-cyclohexen-1-yl phosphoric ester [diethylcyclohexadien - 1,5-yl phosphate, diethyl phenyl phosphate].

2. The cis- and trans-isomers of 2,6-dibromocyclohexanone react differently with triethyl phosphite. The trans-isomer gives the diethylphosphoric ester of the enol form of the ester of cyclohexanone-2-phosphonic-1 acid as the main reaction product. With the cis-form the diethyl ester of cyclohexanone-2-phosphonic-1 acid is formed. In both cases, the products enumerated in paragraph 1 also are obtained.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ESTERS OF β-KETOPHOSPHONIC ACIDS.

COMMUNICATION 9. REACTION OF 2,6-DIBROMO- AND 2,6-DICHLOROCYCLOHEXANONE WITH ONE AND TWO MOLES OF TRIETHYL PHOSPHITE

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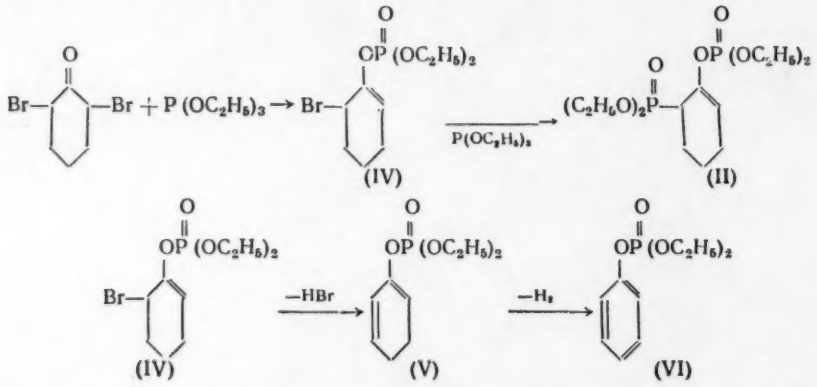
Original article submitted June 8, 1961

In a previous communication we proposed a scheme for the reaction between 2,6-dibromocyclohexanone and two moles of triethyl phosphite to explain the complex course of this reaction (I)



According to this scheme, the bromoester (IV) which is formed initially can react with a second molecule of triethylphosphite to give the expected ester (II), or with splitting out of hydrogen bromide to go over to the diene ester (V), which is easily aromatized to the diethyl phenyl ester of phosphoric acid (VI).

To confirm the correctness of the proposed scheme, it was of interest to stop the reaction at the stage of formation of the bromoester (IV) and to show the possibility of its conversion to the diene ester (V) and the aromatic ester (VI) under the conditions that the reaction was carried out. With this purpose we studied the reaction of 2,6-dibromocyclohexanone with one molecule of triethyl phosphite. The reaction went vigorously and on heating above 130° complete decomposition of the reaction products occurred. Even at a bath temperature below 130° partial decomposition occurred on distillation. Therefore, in order to determine the nature of the products initially formed, we obtained the IR spectra before distillation of the reaction mixture and of the separate fractions of the distillate. The product of reaction of trans-2,6-dibromocyclohexanone (ae) with one molecule of triethyl phosphite before distillation had the IR spectrum shown in Fig. 1, Curve 1; in it the broad absorption band in the region of double bonds consists of superimposed bands with a frequency of 1653 cm^{-1}, which should be related to the diene (V), and a shoulder at about 1680 cm^{-1}, which probably is related to the double bond of the bromoester (IV).

The product of vacuum distillation of the reaction mixture with b.p. 39-42° (2 mm) consisted mainly of cyclohexanone. The fraction with b.p. 81-86° (1.5 mm) in the IR spectrum (Fig. 1, Curve 2) had a very intense absorption band at 1680 cm^{-1}, corresponding to the C=O group of cyclohexanone, and strong bands at 1591 and 1491 cm^{-1}, which are characteristic of the diethyl phenyl ester of phosphoric acid (VI) [1]. Thus, the diene ester (V) on distillation obviously is partially* converted to the phenyl ester (VI).

*The frequency 1655 cm^{-1}, which is characteristic of the diene (III), is overlapped by the intense broad band of cyclohexanone at 1680 cm^{-1}.

Purer products were obtained by treatment of the reaction mixture [2,6-dibromocyclohexanone + 1 M $P(OC_2H_5)_3$] with triethylamine. After separation of the triethylamine hydrobromide from the reaction products, we isolated, on

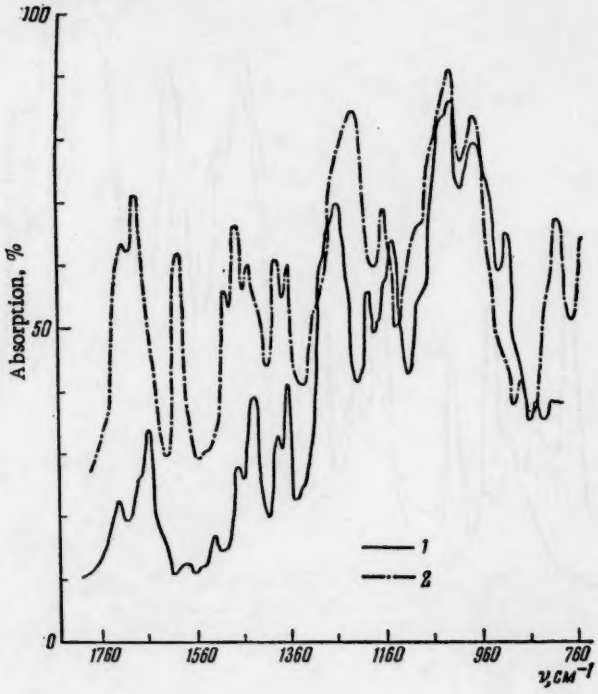


Fig. 1. IR absorption spectra of reaction mixture of 2,6-dibromocyclohexanone + $(C_2H_5O)_3P$ (1 M): 1) before distillation; 2) fraction with b.p. 81-86° (1.5 mm).

distillation, cyclohexanone [b.p. 44-58° (2-3 mm), semicarbazone with m.p. 166-167°, band at 1680 cm^{-1} in the IR spectrum, UV maximum 224 mμ] [2], triethyl phosphate [b.p. 63° (1 mm), $n^{20}D$ 1.4150, IR spectrum], and a fraction with b.p. 105-110° (1 mm), $n^{20}D$ 1.4775, d^{20}_{20} 1.1406. With respect to its analysis for phosphorus and its IR spectrum, this fraction coincided with the fraction with b.p. 104-107° (2.5 mm) which was obtained by the action on 2,6-dibromocyclohexanone (trans-form) of two molecules of triethyl phosphite [1]. The IR spectrum of the fraction with b.p. 105-110° (1 mm) is given in Fig. 2, Curve 1, and the UV spectrum in Fig. 3. In the IR spectrum there are the frequency 1655 cm^{-1}, which indicates the presence of the diene (V), and the frequency 1591 cm^{-1}, which indicates the presence of the phenyl ester (VI).

In the UV spectrum of this fraction there is an absorption maximum at 262.5 mμ (log k 3.64), which is characteristic of the 1,3-cyclohexadiene system [3]. The presence of a conjugated system in the fraction with b.p. 105 to 110° (1 mm) was verified by treating it with maleic anhydride. A fraction was obtained with b.p. 118-119° (2 mm), in the IR spectrum of which (Fig. 2, Curve 2) there appeared, instead of the frequency of the diene bond at 1655 cm^{-1}, absorption bands of the anhydride group at 1777 (s) and 1846 (w) [4], and the bands at about 1680 and 1591 cm^{-1} for the diethyl bromo-6-cyclohexen-1-yl and diethyl phenyl esters of phosphoric acid were preserved, which were found accordingly in the spectrum of the product with b.p. 105-110° (1 mm) before treatment with maleic anhydride (Fig. 2, Curve 1).

As can be seen from our statement, the data obtained are in complete agreement with the previously proposed scheme for the reaction of 2,6-dibromocyclohexanone with triethyl phosphite. Also in accordance with the scheme presented were experiments that we set up on the action of triethyl phosphite (2 M) on 2,6-dichlorocyclohexanone (trans- and cis-forms). In this case, half of the phosphite used was recovered. From the reaction products we isolated,

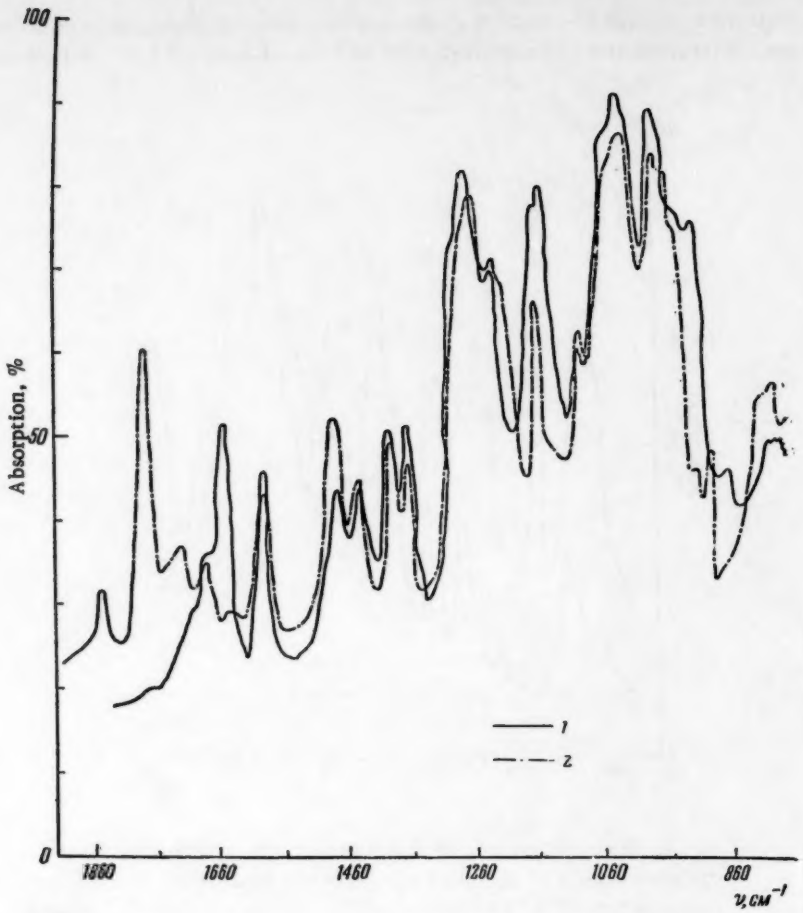


Fig. 2. IR absorption spectrum of fraction with b.p. 105-110° (1 mm) before and after treatment with maleic anhydride: 1) fraction with b.p. 105-110° (1 mm); 2) ester with b.p. 118-119° (2 mm).

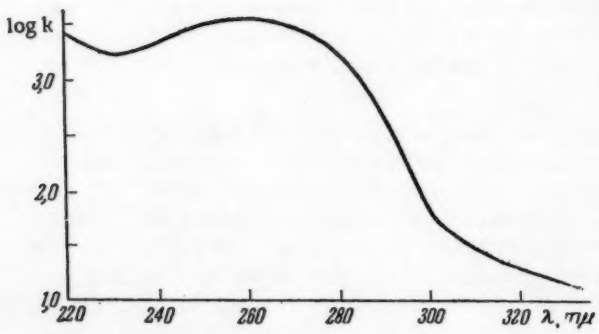


Fig. 3. UV absorption spectrum of fraction with b.p. 105 to 110° (1 mm) in CH_3OH.

in 70% yield, diethyl chloro-6-cyclohexen-1-yl phosphoric ester (IV) (in the place of the bromine there is an atom of chlorine) with the following constants: b.p. 141° (2 mm); n^{20} 1.4700; d^{20}_0 1.1984; MR 62.56: for $C_{10}H_{18}O_4PCl$; calculated MR 63.09.

The Raman spectrum had the following frequencies (cm^{-1}):

173 (3b),* 216 (2), 272 (2), 330 (1), 373 (1), 472 (2), 515 (2), 533 (5b), 577 (2), 14 (3), 642 (1), 695 (5), 712 (6), 748 (6b), 785 (1), 818 (2), 852 (2), 890 (2), 912 (3), 936 (3), 982 (3), 1035 (4), 1084 (5), 1100 (4), 1152 (2), 1183 (2), 1230 (5), 1260 (2), 1293 (5), 1337 (2), 1348 (1), 1373 (5), 1395 (1), 1436 (6), 1452 (4), 1476 (1), 1620 (1), 1673 (8), 2727 (1), 2842 (4), 2873 (4), 2900 (3b), 2933 (7), 2974 (5b), 3060 (2).

*b = broad line.

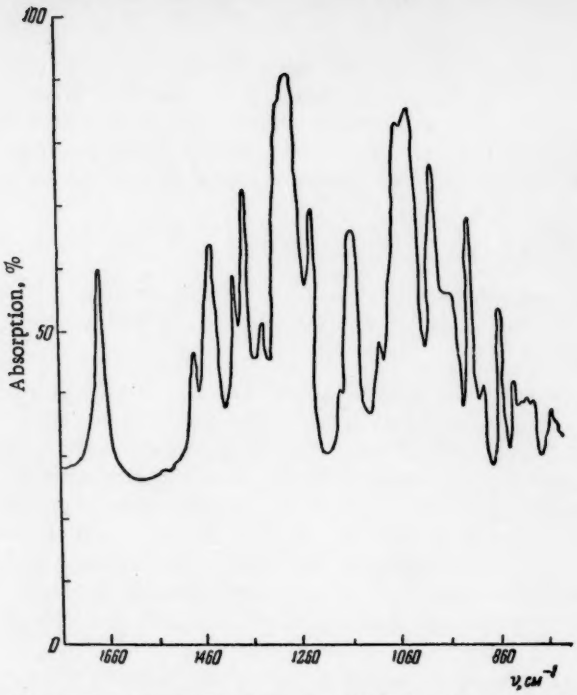


Fig. 4. IR absorption spectrum of diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid.

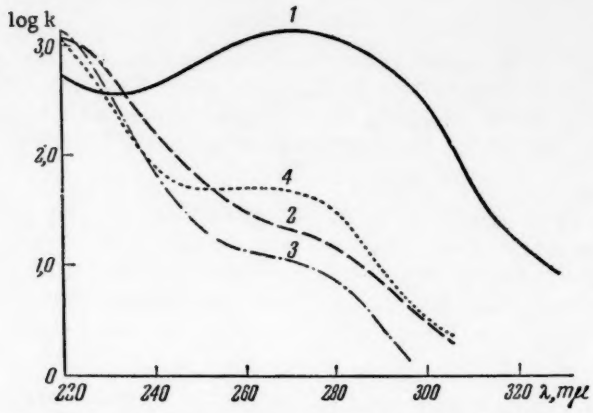


Fig. 5. UV absorption spectra in CH_3OH: 1) fraction with b.p. 107-114° (1.5 mm). Diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid. 2) With b.p. 141° (2 mm); 3) with b.p. 132° (1 mm); 4) after transesterification.

In the IR spectrum of the diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid (Fig. 4) there was a band at 1672 cm^{-1} for the C=C group and a wide intense band for the P=O group with maxima at 1279 and 1231 cm^{-1}. As follows from the results obtained, because of the lower reactivity of chlorine in comparison with bromine, in the case of dichlorocyclohexanone the product with only one chlorine atom was formed smoothly in the reaction with the phosphite. An attempt to replace the second atom of chlorine by the action of a second molecule of triethyl phosphite on the monochloride under more severe conditions (temperature up to 210°) did not lead to product (II).

Upon heating, hydrogen chloride was split out with the formation of the diene compound [b.p. 107 to 114° (1.5 mm)], d^{20}_0 1.1171, $n^{20}D$ 1.4523; its UV spectrum had an absorption maximum at 270 mμ (log k 3.1) (Fig. 5, Curve 1). In view of the small amounts, we did not investigate it in more detail. When the cis-isomer of 2,6-dichlorocyclohexanone was reacted with triethyl phosphite (2 M) the same results were obtained as with the trans- isomer. The constants of the monochloride obtained, and its Raman, IR and UV spectra (Fig. 5, Curve 3) coincided completely with those obtained from the trans-isomer (Fig. 5, Curve 2). The diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid did not transesterify with ethyl alcohol in the presence of metallic sodium or H_3PO_4. On the basis of the UV spectral data (Fig. 5, Curve 4), it may be considered that in transesterification in the presence of sodium alcoholate splitting out of hydrogen chloride occurs to a small extent with the formation of the diene compound (V) (small maximum at about 270 mμ). The instability of the bromoester (IV) and the ease of splitting out hydrogen bromide make understandable the small yields of the ester of cyclohexanone-2-phosphonic acid obtained in our experiments on the bromination of the diethyl cyclohexenyl phosphoric ester with bromosuccinimide [5] and in the reaction of cis-2,6-dibromocyclohexanone with triethyl phosphite [1].

When the diethyl cyclohexenyl ester of phosphoric acid was brominated with bromosuccinimide, by analogy with the data of Machinskii and Barkhash [6] for the bromination of cyclohexenyl acetate with bromosuccinimide, where 6-bromocyclohexen-1-yl-1 acetate was obtained, we should have obtained the bromide (IV). Bromide (IV) can react with triethyl phosphite to give (II), or can undergo conversions indicated in the diagram given at the beginning of this article.

A detailed study of the products obtained in this reaction permitted isolation of diethylphosphorous acid, triethyl phosphate, and a fraction with b.p. 113-114° (2 mm), d^{20}_0 1.1216, $n^{20}D$ 1.4613, which had constants close to those of the diethyl ester of cyclohexanone-2-phosphonic acid. A study of its IR and Raman spectra showed that it contained the diethyl ester of cyclohexanone-2-phosphonic acid (frequencies 1712, 1634, and 1162 cm^{-1}), the

diethyl cyclohexenyl ester of phosphoric acid used in the bromination reaction (frequencies 1685 and 1138 cm^{-1}), diethyl cyclohexadienyl phosphate (V) (frequencies 1655 and 1148 cm^{-1}), and the diethyl phenyl ester of phosphoric acid (VI) (frequencies 1591 and 1490 cm^{-1}).

From the higher fractions we isolated a fraction with b.p. 140-143° (2.5 mm) which contained 13% bromine and 14.88% phosphorus. The fraction probably was a mixture of the bromide (IV) and its isomer diethyl 3-bromocyclohexen-1-yl-1 ester of phosphoric acid, with tetraethyl hypophosphate. We did not isolate a fraction corresponding to product (II). Thus, the reaction of the product of bromination of the diethyl cyclohexenyl ester of phosphoric acid by bromosuccinimide with triethyl phosphite proceeded similarly to the reaction of cis-2,6-dibromocyclohexanone with triethyl phosphite [1].

EXPERIMENTAL

The UV spectra were determined in an SF-4 quartz spectrophotometer. The IR spectra were determined for a capillary film of liquid in a Hilger H-800 spectrograph. The Raman spectra were measured in an ISP-51 spectrograph from the 4358 A excited blue line of a mercury lamp.

Reaction of trans-2,6-dibromocyclohexanone with triethyl phosphite (1M:1M). To 48 g of freshly distilled 2,6-dibromocyclohexanone with b.p. 118-120° (2 mm), $n^{20}D$ 1.5628 was added dropwise, with cooling, 31 g of triethyl phosphite. After one day the mixture was heated for 2 hr. The temperature of the bath was gradually brought to 130°. In this process 14.6 g of ethyl bromide (theoretical amount 20.4 g) was distilled off. The remaining ethyl bromide was drawn off with suction from the reaction mixture, after it had been cooled, with a water pump under slight heating. The mixture was a light yellow in color and gave no coloration with $FeCl_3$. The reaction mixture was divided into three portions. Vacuum distillation of the first portion at a bath temperature of 170° proceeded with violent decomposition and resinification. Distillation of the second portion was carried out at a bath temperature not higher than 130°. The following fractions were obtained: I) b.p. 39-42° (1.5 mm); II) b.p. 81-86° (1.5 mm) with a phenol odor, the color of strong tea, quickly darkening in the air and thickening on standing. A Beilstein test for halogen was positive; no color was given with $FeCl_3$. Distillation proceeded with decomposition; in the flask there was a large amount of undistilled residue. III) The third portion of the mixture was treated, without distillation, with triethylamine. To 16 g of the mixture in 40 ml of dry ether was added dropwise 8 g of triethylamine (50% excess). The mixture did not heat up. The mixture was further heated, first on a water bath with a reflux condenser for 8 hr (1.5 g of triethylamine hydrobromide was formed), then in a sealed tube at 90° for 20 hr. A total of 4.6 g (50% of theory) of triethylamine hydrobromide separated out.

Upon distillation of the mixture after separation of the precipitate, the following fractions were obtained: I) b.p. 44-58° (2 mm), which yielded a semicarbazone with m.p. 166-167° [2]; II) b.p. 63° (1 mm), $n^{20}D$ 1.4150, triethyl phosphate identified by its IR spectrum; III) b.p. 105-110° (1 mm), d^{20}_{20} 1.1406, $n^{20}D$ 1.4775; found MR 57.58. Found: P 12.20, 12.30%. $C_{10}H_{19}O_4P$. Calculated: P 13.24%. IV) b.p. 110-112° (1 mm), d^{20}_{20} 1.579, $n^{20}D$ 1.4715. There was a large amount of tarry residue in the flask.

Fractions (III) and (IV) were further treated with maleic anhydride. To 1.2 g of material was added 0.5 g of freshly distilled maleic anhydride. The mixture was heated for 10 min. on a water bath to complete solution of the maleic anhydride. The mixture thickened and greatly darkened. It did not crystallize on cooling. Distillation in a special umbrella-type flask gave the following fractions: I) b.p. 67-71° (3 mm), with a sharp phenolic odor, yielding tribromophenol on treatment with bromine water; II) b.p. 118-119° (2 mm), $n^{20}D$ 1.4520. There was a considerable amount of undistilled residue in the flask.

Reaction of 2,6-dichlorocyclohexanone with triethyl phosphite (1M:2M). 2,6-Dichlorocyclohexanone was prepared by the action of sulfuryl chloride on 2-chlorocyclohexanone [7]. On distillation of the reaction mixture, cis-2,6-dichlorocyclohexanone was obtained with b.p. 119° (3 mm), crystallizing on standing. Recrystallization from ether gave white crystals which darkened on standing, with m.p. 72-72.5° [8]. By distillation of the lower fractions on a column of 17 theoretical plates we obtained gem-2,6-dichlorocyclohexanone with b.p. 65.5-69° (2 mm), $n^{15}D$ 1.4970, d^{15}_4 1.2983 [8]. The Raman spectrum of the gem-isomer had the following frequencies (cm^{-1}):

188 (4b), 233 (6), 279 (4), 287 (5), 303 (2), 333 (0), 360 (9), 429 (3), 298 (8), 568 (10), 647 (1), 738 (5b), 806 (4), 838 (4), 859 (4), 948 (2), 992 (3), 1023 (0), 1056 (7), 1083 (4d),* 1118 (2), 1144 (1), 1223 (2), 1259 (4), 1271 (4), 1318 (2), 1337 (2), 1432 (5), 1452 (6), 1659 (1), 1683 (1), 1744 (6), 2660 (0), 2818 (0), 2853 (3), 2876 (6), 2917 (10), 2959 (10b).

*d = double line.

Gem-2,6-dichlorocyclohexanone was isomerized in glacial acetic acid containing HCl [8]. After the isomerization a small fraction of the cis-form was isolated. By distillation of the liquid portion on a column of 17 theoretical plates trans-2,6-dichlorocyclohexanone was obtained with b.p. 82-82.5° (2.5 mm), $n^{15}D$ 1.5067, d^{15}_4 1.3198 [8]. The Raman spectrum of 2,6-dichlorocyclohexanone with b.p. 82-82.5° (2.5 mm) had the following frequencies (cm^{-1}):

225 (3), 260 (2), 282 (1), 319 (3), 333 (6), 362 (1), 432 (1), 456 (6), 489 (6), 526 (0), 586 (5), 667 (5b), 696 (4), 787 (3), 810 (2), 855 (2), 873 (4), 936 (1), 972 (4), 1032 (2), 1057 (2), 1079 (4), 1102 (1), 1158 (2), 1615 (2), 1653 (3), 1691 (2), 1734 (4), 2842 (2), 2872 (5), 2910 (4b), 2929 (4), 2959 (6b), 2988 (5).

To 34.7 g of 2,6-dichlorocyclohexanone with b.p. 82-82.5° (2.5 mm) (trans-form) was added dropwise, with cooling, 69 g of triethyl phosphite. When the first half of the triethyl phosphite was added, strong evolution of heat by the reaction mixture was observed; addition of the second half did not cause heating. The mixture was heated on an oil bath for 1.5 hr; the temperature of the bath at the end of the experiment was brought up to 180°. Upon vacuum distillation, 32 g of triethyl phosphite was recovered with b.p. 49-51° (11 mm), d^{20}_0 0.9660, $n^{20}D$ 1.4115. As a result of several redistillations of the higher fractions, we obtained the diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid with b.p. 141° (2 mm), $n^{20}D$ 1.4700, d^{20}_0 1.1984 (50.4 g); yield 70%. Found: P 11.79, 11.81; Cl 13.12, 13.17%. MR 62.56. $C_{10}H_{18}O_4PCl$. Calculated: P 11.54; Cl 13.19%. MR 63.09.

The reaction of triethyl phosphite with cis-2,6-dichlorocyclohexanone with m.p. 72-72.5°, carried out under the same conditions, proceeded similarly to the experiment with trans-2,6-dichlorocyclohexanone. Somewhat less evolution of heat by the reaction mixture was observed. From the reaction we recovered 50% of the triethyl phosphite unreacted. The diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid was obtained with b.p. 132° (1 mm), $n^{20}D$ 1.4701, d^{20}_0 1.1989. Transesterification of the diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid (19 g) was carried out with absolute ethyl alcohol (30 ml) in the presence of metallic sodium (0.3 g). The mixture was heated for 2 hr on a water bath. Upon distillation the following fractions were obtained: I) b.p. 67° (24 mm), 1 g; II) b.p. 72-81° (3.5 mm), 2.1 g; III) b.p. 150-153° (3.5 mm), 14.8 g. Fraction III was again treated, first with an alcoholic solution of C_2H_5ONa, whereupon the mixture was heated for 6 hr on a water bath, and then with absolute ethyl alcohol in the presence of H_3PO_4 with heating for 6 hr on a water bath. Upon distillation the following fractions were obtained: I) b.p. 53-65° (3 mm), small amount; II) b.p. 141-141.5° (2.5 mm), 7.5 g, d^{20}_0 1.1677, $n^{20}D$ 1.4640. Found: P 11.83, 11.65%.

Action of triethyl phosphite on diethyl chloro-6-cyclohexen-1-yl phosphoric acid. A mixture of 5 g of diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid with b.p. 141° (2 mm) and 3.1 g of triethyl phosphite was heated in an Arbuzov flask for 4 hr at a temperature of 205-215°. Ethyl chloride was evolved. Upon distillation the fractions obtained were: I) b.p. 59-60° (2 mm), 2.8 g, d^{20}_0 1.0609, $n^{20}D$ 1.4080, diethylphosphorous acid; II) b.p. 107 to 114° (1.5 mm), 0.8 g, d^{20}_0 1.1171, $n^{20}D$ 1.4523, containing no halogen, giving no color with $FeCl_3$.

Action of triethyl phosphite on the product of bromination of diethyl cyclohexenyl phosphate with bromosuccinimide. To a solution of 47 g of diethyl cyclohexenyl ester of phosphoric acid in 50 ml of dry CCl_4 was added in portions, with stirring, 35.7 g of bromosuccinimide. The mixture was heated on a water bath at a temperature not higher than 85° until the bromosuccinimide dissolved. After one day, 17.3 g of succinimide was filtered off (theoretical amount 19.9 g); the solvent was distilled off in vacuum. The residue was washed several times with water and dried with Na_2SO_4. The product was not distilled.

To 51 g of the product obtained was added dropwise 27 g of triethyl phosphite. The reaction mixture did not evolve heat. The mixture was heated on an oil bath for 2.5 hr; the temperature at the end of the experiment was brought up to 185°. Ethyl bromide (13.3 g) distilled off (theoretical amount 17.7 g). As a result of several fractional distillations with a Widmer dephlegmator, the following fractions were obtained: I) b.p. 53-59° (2.5 mm), 7 g; II) b.p. 65-78° (3 mm), 10 g, $n^{20}D$ 1.4155; III) b.p. 113-114° (2 mm), 10.5 g, $n^{20}D$ 1.4613, d^{20}_0 1.1216, containing no halogen, giving an intense lilac color with $FeCl_3$ in CH_3OH; IV) b.p. 140-143° (2.5 mm), 5 g, $n^{20}D$ 1.4495, d^{20}_0 1.2393. The fraction was again distilled: b.p. 133-136° (1.5 mm), $n^{20}D$ 1.4520, d^{20}_0 1.2462. Found: Br 13.22, 13.08; P 14.73, 15.02%. $C_{10}H_{18}O_4PBr$. Calculated: Br 25.52; P 9.91%.

SUMMARY

1. The reaction of trans-2,6-dibromocyclohexanone with one and two molecules of triethyl phosphite follows a complex course. The reaction with one molecule of triethyl phosphite stops at the stage of formation of the diethyl bromo-6-cyclohexen-1-yl ester of phosphoric acid, which is further converted to diethyl cyclohexadien-1,3-yl-2 phosphate and diethyl phenyl phosphate. The diethyl phosphoric ester of the enol form of the ester of cyclohexanone-2-phosphonic-1 acid is not produced in this process.

2. The cis- and trans-isomers of 2,6-dichlorocyclohexanone react with two molecules of triethyl phosphite with the formation of diethyl chloro-6-cyclohexen-1-yl ester of phosphoric acid.

3. The bromination of the diethyl cyclohexenyl ester of phosphoric acid with bromosuccinimide with subsequent treatment with triethyl phosphite does not lead to the diethylphosphoric ester of the enol form of cyclohexanone-2-phosphonic-1 acid. A mixture of products is formed similar to the mixture obtained when triethyl phosphite acts on cis-2,6-dibromocyclohexanone.

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SYNTHESIS OF DIPHENYLVINYLPHOSPHINE OXIDE

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We recently reported the synthesis of diethyl-, dipropyl-, and ethylphenyl-vinylphosphine oxides [1]. Some tertiary vinylphosphine oxides were synthesized by one of us with Chzhan Zhun-yui and Tsevetkov [2]. We synthesized diphenylvinylphosphine oxide as follows:

$$C_6H_5PCl_2 \xrightarrow[t^\circ]{AlCl_3} (C_6H_5)_2PCl \xrightarrow{CH_2-CH_2 \diagdown O \diagup} (C_6H_5)_2POCH_2CH_2Cl \xrightarrow{t^\circ}$$

$$\longrightarrow (C_6H_5)_2P(O)CH_2CH_2Cl \xrightarrow{-HCl} (C_6H_5)_2P(O)CH=CH_2 .$$

The first stage of the synthesis, the conversion of dichlorophenylphosphine into chlorodiphenylphosphine, was carried out by the catalytic disproportionation of dichlorophenylphosphine in presence of aluminum chloride with continuous removal of the phosphorus trichloride formed by distillation:

$$2\ C_6H_5PCl_2 \xrightarrow[t^\circ]{AlCl_3} (C_6H_5)_2PCl + PCl_3 .$$

Chlorodiphenylphosphine is formed in 70% yield. The method is simple and readily reproducible [3,4].* In an analogous way we have prepared chloroditolylphosphine in 65% yield.

The second stage of the synthesis, the reaction of chlorodiphenylphosphine with ethylene oxide, was carried out by the passage of a stream of ethylene oxide into chlorodiphenylphosphine. It should be noted that the union of two phenyl groups to the tervalent phosphorus atom lowers the reactivity of the P–Cl bond. Phosphorus trichloride reacts the most vigorously with ethylene oxide [5], dichlorophenylphosphine reacts with it somewhat less vigorously [1,6], but the reaction with chlorodiphenylphosphine, though exothermic, requires heating to 60° for 1 hr for its completion.

The third stage of the synthesis, the isomerization of 2-chloroethyl diphenylphosphinite into (2-chloroethyl)-diphenylphosphine oxide, does not proceed smoothly. Depending on the reaction conditions (atmospheric pressure or vacuum), variable amounts of (2-chloroethyl)diphenylphosphine oxide and ethylenebis(diphenylphosphine) dioxide $(C_6H_5)_2P(O)CH_2CH_2P(O)(C_6H_5)_2$ are formed.

The formation of ethylenediphosphine derivatives has been observed previously. Thus, one of us found that, in the isomerization of aromatic esters of 2-chloroethyl dihydrogen phosphite the main product was tetraaryl ethylenediphosphonate [7]. We observed the formation of dioxides in the isomerization of 2-chloroethyl dialkylphosphinites [1].

Further, in the isomerization of 2-chloroethyl diphenylphosphinite, as a result of spontaneous dehydrochlorination, the two above-mentioned products are accompanied by diphenylvinylphosphine oxide. If the reaction product is treated with alkali, diphenylvinylphosphine oxide becomes the main reaction product. The third and fourth stages of the synthesis are thus combined.

* We worked out this method in 1960, but did not publish it in view of the appearance of the communications [3] and [4].

To verify the structure of the oxide obtained we carried out a confirmatory synthesis from vinylphosphonic dichloride and phenylmagnesium bromide:

$$CH_2=CH—POCl_2 + 2C_6H_5MgBr \rightarrow CH_2=CH—P(O)(C_6H_5)_2 + 2MgBrCl.$$

EXPERIMENTAL

Chlorodiphenylphosphine. Dichlorophenylphosphine (72 g, 0.4 mole) was heated in a weak stream of nitrogen in presence of 3 g (4% by weight) of anhydrous aluminum chloride in an apparatus which enabled the phosphorus trichloride formed to be fractionated off. As the reaction proceeded, the bath temperature was raised (from 220° to 300°) so as to keep the reaction mixture at the boil. Heating was stopped after the liberation of about 0.2 mole of phosphorus trichloride (this required about 2 hr). The residue was vacuum-fractionated. We obtained 31 g (70%) of chlorodiphenylphosphine; b.p. 119-120° (1 mm), $n^{20}D$ 1.6360, d^{20}_4 1.1935; m.p. 14-16°. The literature [8] gives: b.p. 111-112° (0.3 mm), $n^{20}D$ 1.6361.

Chloroditolylphosphine. This was prepared analogously by the disproportionation of dichlorotolylphosphine at 240-320°; yield 65%; b.p. 132-133° (1 mm), $n^{20}D$ 1.6190, d^{20}_4 1.1470. Found: C 67.0, 67.0; H 5.7, 5.8; P 12.4, 12.4; Cl 14.6, 14.6%. $C_{14}H_{14}PCl$. Calculated: C 67.6; H 5.7; P 12.4; Cl 14.3%. The melting point of methyldi-p-tolylphosphine prepared from chlorodi-p-tolylphosphine was 143-144°. The literature [9] gives m.p. 143-144°.

2-Chloroethyl diphenylphosphinite. Dry ethylene oxide was passed into a stirred solution of 22.0 g (0.1 mole) of chlorodiphenylphosphine in 40 ml of dry benzene; in the course of 30 min the temperature of the reaction mixture rose to 60° and then began to fall. Ethylene oxide was passed further for 1 hr with heating of the reaction flask (bath temperature about 60°). After removal of solvent in a vacuum we obtained 2-chloroethyl diphenylphosphinite, which we succeeded in solidifying by cooling; the yield was quantitative; m.p. 26-27° (from hexane). Found: C 64.0, 64.0; H 5.5, 5.4; P 11.6, 11.9; Cl 13.2, 13.4%. $C_{14}H_{14}POCl$. Calculated: C 63.5; H 5.3; P 11.7; Cl 13.4%.

Diphenylvinylphosphine oxide and ethylenebis(diphenylphosphine) dioxide. 2-Chloroethyl diphenylphosphinite (7.9 g, 0.03 mole) was heated in a vacuum (10 mm) in a stream of nitrogen at about 160° for 90 min. When cool, the reaction mixture crystallized out; the loss in weight was 0.6 g. The crystalline mass was ground to a powder and rubbed out with 15 ml of acetone; 15 ml of ether was then added, and the undissolved precipitate of ethylenebis-(diphenylphosphine) dioxide was filtered off. After recrystallization from alcohol: m.p. 269-270°; yield 0.7 g (11%). Found: C 72.3, 72.2; H 5.6, 5.5; P 14.3, 14.3; no Cl. $C_{26}H_{24}P_2O_2$. Calculated: C 72.5; H 5.6; P 14.4%.

Solvent was removed from the filtrate after the separation of the dioxide; the residue was dissolved in 30 ml of absolute alcohol and treated, with cooling with ice water, with an alcoholic solution of potassium hydroxide (1 mg of KOH in 30 ml of alcohol). The potassium chloride that separated (0.9 g) was filtered off, alcohol was removed in a vacuum, and the residue was dissolved in benzene and washed with water. On evaporation of the benzene solution there separated crystals of diphenylvinyl oxide, yield 4.8 g (70%); m.p. 116-117°. Found: C 73.7, 73.7; H 5.9, 5.7; P 13.6, 13.7%. $C_{14}H_{13}PO$. Calculated: C 73.7; H 5.7; P 13.6%.

When 2-chloroethyl diphenylphosphinite (5.3 g) was heated with stirring at atmospheric pressure in nitrogen at a bath temperature of about 130°, there was a sharp rise of temperature (to 230°) and foaming accompanied by the distillation of dichloroethane and the liberation of hydrogen chloride. The reaction mixture was heated further for 30 min at 160°. After treatment analogous to that described above, we obtained 1.3 g (30%) of ethylenebis(diphenylphosphine) dioxide and 2.1 g (46%) of diphenylvinylphosphine oxide.

Preparation of diphenylvinylphosphine oxide from vinylphosphonic dichloride and phenylmagnesium bromide. Dropwise addition was made of a solution of 14.5 g (0.1 mole) of vinylphosphonic dichloride in 60 ml of ether to a stirred and cooled (0°) solution of phenylmagnesium bromide prepared from 5.0 g (0.21 g-atom) of magnesium and 33.0 g (0.21 mole) of bromobenzene in 150 ml of ether. The reaction mixture was then boiled for 1 hr, cooled, and treated with stirring with 80 ml of a 20% solution of ammonium chloride. On the next day the ether layer was separated, 50 ml of water and 100 ml of benzene were introduced into the reaction flask, and the mixture was stirred with boiling of the benzene for 1 hr. The benzene layer was separated and combined with the ether layer, and the whole was dried with sodium sulfate. After removal of solvent in a vacuum and recrystallization from benzene, we obtained large well-formed crystals of diphenylvinylphosphine oxide, amounting to 3.5 g (15%); m.p. 116-117°. Found: C 73.4, 73.4; H 5.6, 5.8; P 13.9, 14.0%. $C_{14}H_{13}PO$. Calculated: C 73.7; H 5.7; P 13.6%. A mixture test with the sample of oxide prepared by the previous method showed no depression of melting point.

SUMMARY

Diphenylvinylphosphine oxide [and ethylenebis(diphenylphosphine) dioxide] were synthesized in accordance with the scheme:

$$PCl_3 \rightarrow C_6H_5PCl_2 \rightarrow (C_6H_5)_2PCl \rightarrow (C_6H_5)_2POCH_2CH_2Cl \rightarrow$$

$$\rightarrow (C_6H_5)_2P(O)CH_2CH_2Cl \rightarrow (C_6H_5)_2P(O)CH{=}CH_2 .$$

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ISOMERIZATION OF FREE ALKYL RADICALS IN SOLUTION

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The question of the existence of isomerization reactions of free radicals, as a general property of free radicals, was first raised in the papers of Semenov and co-workers [1]. Nalbadyan and Fok [2], who studied the photochemical oxidation of hydrocarbons, sensitized with mercury in a jet at above 100°, concluded that intermediate isomerization of peroxy radicals occurred, e.g.,

$$CH_3—O—O^{\cdot} \rightarrow {}^{\cdot}CH_2—O—OH\,.$$

The conclusion that the isomerization of free alkyl radicals occurs in the gas phase even at room temperature appears to follow from the experiments of Voevodskii and Mardaleishvili [3] on the exchange reactions of propyl, isobutyl-, and cyclohexyl radicals with deuterium. The view that isomerization (β-isomerization) occurred was reached in explanation of the fact that the recombination products were strongly deuterated (up to 50%). Nesmeyanov and Freidlina and co-workers [4] discovered isomerization in solutions of peculiar free radicals of the type

$$CCl_3—{}^{\cdot}C\begin{matrix}X\\CH_2Y\end{matrix} \rightarrow \dot{C}Cl_2—\underset{Cl}{\overset{X}{C}}—CH_2Y,$$

in which X and Y = H and Cl, H, and Br, H and CCl_3, CH_3 and Br, CH_3 and Cl, Cl and Br, Cl and Cl, Br and Br.

The question of the ability of free alkyl radicals to isomerize in solution remained open. Moreover, all investigation yet undertaken with the object of detecting the isomerization of alkyl radicals in solutions have given only negative results. Thus, Kharasch [5], in a study of the decomposition of butyryl and isobutyryl peroxides in carbon tetrachloride,

$$(CH_3—CH_2—CH_2—COO)_2 \xrightarrow{CCl_4} CH_3—CH_2—CH_2—Cl\,; \qquad (1)$$

$$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—COO\right)_2 \xrightarrow{CCl_4} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—Cl\,. \qquad (2)$$

did not detect even traces of isopropyl chloride in the first reaction or of propyl chloride in the second. The conclusion of the absence of the isomerization of free radicals in solutions was reached also by de Tar, who studied the decomposition of 5-phenylvaleryl peroxide in carbon tetrachloride and benzene [6,7]. The character of all the final products isolated by de Tar indicates that the radical $C_6H_5—CH_2—CH_2—CH_2^{\cdot}$ does not isomerize. However, if free alkyl radicals formed, for example, by the decomposition of diacyl peroxides in solution, actually exist as kinetically independent particles, they must be capable of isomerization.

It is known that free alkyl radicals in solution are capable of abstracting hydrogen atoms from solvent molecules:

$$R^{\cdot} + H:C\!\!<\!\!\!\!\!\!\!\!\rightarrow R—H + \dot{C}\!\!<\!\!\!\!\!\!\!\!\rightarrow\,.$$

There is no reason to suppose that free alkyl radicals in solution are not able to abstract hydrogen atoms from themselves with change in valence, if there are suitable steric conditions. The extent of the isomerization of a free radical will depend on the relation between the rates of the isomerization and substitution reactions. For the decomposition of peroxides in solvents at moderate temperatures we must take account of the possibility of isomerization of free radicals to a small extent, which may be detected only with very accurate methods of investigation.

In view of these considerations, we studied the decomposition of butyryl peroxide,* labeled in the α-position with radiocarbon C^{14}, in boiling carbon tetrachloride [8]:

$$(CH_3-CH_2-C^{14}H_2-COO)_2+2CCl_4 \rightarrow 2CH_3-CH_2-CH_2-Cl+2CO_2+CCl_3-CCl_3 .$$

To establish the position of the C^{14} atom in the propyl chloride molecule, the latter was hydrolyzed to propyl alcohol, and propionic acid was oxidized to acetic acid**

$$CH_3-CH_2-CH_2-Cl \xrightarrow[(K_2CO_3)]{H_2O} CH_3-CH_2-CH_2-OH \xrightarrow{KMnO_4}$$

$$\rightarrow CH_3-CH_2-COOH \xrightarrow{K_2Cr_2O_7} CH_3-C\begin{matrix}O\\OH\end{matrix} .$$

The acetic acid was found to be active (about 4% of the activity of the propionic acid). It follows from this fact that part of the propyl radicals underwent rearrangement.

To establish the position of the C^{14} in the acetic acid molecule, we carried out, on the one hand, fusion of its sodium salt with alkali and, on the other, Schmidt cleavage:

$$CH_3-C\begin{matrix}O\\ONa\end{matrix} +NaOH \rightarrow Na_2CO_3+C^{14}H_4 ; \qquad (a)$$

$$CH_3-C\begin{matrix}O\\OH\end{matrix} +HN_3 \rightarrow C^{14}H_3-NH_2+CO_2 . \qquad (b)$$

We showed that, in the first case, the sodium carbonate formed was inactive, and, in the second case, the whole of the activity passed from the acetic acid to the methylamine.

It is clear from these results that the free propyl radical formed in the thermal decomposition of butyryl peroxide in solution

$$(CH_3-CH_2-CH_2-COO)_2 \rightarrow 2CH_3-CH_2-CH_2^{\cdot}+2CO_2,$$

undergoes isomerization of the type

$$CH_3-CH_2-C^{14}H_2^{\cdot} \rightleftarrows {}^{\cdot}CH_2-CH_2-C^{14}H_3.$$

From the values of the activities of acetic acid and methylamine found in three experiments, it follows that under the given conditions isomerization of the propyl radical proceeds to the extent of 4 ± 0.5%.***

*Butyryl peroxide labeled with C^{14} at the α-carbon atom was synthesized as follows: $CH_3-CH_2-C^{14}H_2-OH \xrightarrow{Br_2+P} CH_3-CH_2-C^{14}H_2-Br \xrightarrow[(2)\ \text{hydrolysis}]{(1)\ NaCN} CH_3-CH_2-C^{14}H_2-COOH \xrightarrow[(2)\ Na_2O_2]{(1)\ SOCl_2} (CH_3-CH_2-C^{14}H_2-COO)_2$.

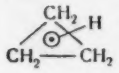
**It was shown by special experiments (see Experimental) that propyl-1-C^{14} alcohol used as starting material in the synthesis of butyryl peroxide labeled with C^{14} at the α-carbon atom contained C^{14} only in the 1-position; also, that in the synthesis of propyl-1-C^{14} bromide and butyric-2-C^{14} acid and in the hydrolysis of propyl chloride and the oxidation of propionic acid no rearrangement occurs.

***According to Lorber and Cook [9], on oxidation of propionic-2-C^{13}, 3-C^{14} acid with potassium dichromate, the carbon dioxide formed contains not only C^{12}, but also some of the C^{13} and C^{14} (it appears that the propionic acid is in part oxidized to beyond the acetic acid stage). It is clear that these results do not require that any corrections should be made in the present work, as we investigated the activity of the acetic acid, not the carbon dioxide.

In an examination of the probable mechanism of the isomerization of the propyl radical we must, first of all, reject the possibility of two-stage migration of a hydrogen atom from the α-position.

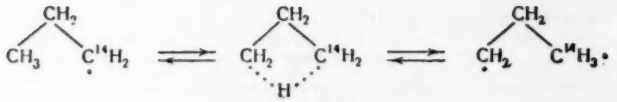
$$CH_3—CH_2—C^{14}H^{\cdot}_2 \rightleftarrows CH_3—CH—C^{14}H_3 \rightleftarrows {}^{\cdot}CH_2—CH_2—C^{14}H_3.$$

Evidence against such a mechanism is provided both by steric considerations and by the results of Kharasch's experiments [5], which did not reveal even traces of isopropyl chloride in the decomposition of butyryl peroxide in carbon tetrachloride. Another view that is contrary to the experimental results is that of the intermediate formation of a nonclassical radical



which would be a peculiar complex of cyclopropane and a hydrogen atom. In this case, the rupture of each of the three C – C bonds (on reaction with CCl_4) of the cyclopropane ring is equally probable, so that the distribution of C^{14} should be uniform in the propyl chloride over all the three positions in the propyl group. Actually, C^{14} is found only in the 1- and 3-positions.

It is most probable that the isomerization proceeds through a four-membered cyclic transition state (A) in one stage:



(A)

It is interesting to note that the propyl cation formed by the action of nitrous acid on propylamine perchlorate does not undergo skeletal rearrangement, as was considered earlier [10], but is isomerized as a result of the migration of a hydrogen atom [11] in a way analogous to that found in the propyl radical.

In view of our results on the isomerization of the propyl radical in solution, it would be interesting to understand why de Tar [6,7] did not observe the isomerization of 4-phenylbutyl under conditions that were the same as ours.

$$C_6H_5—CH_2—CH_2—CH_2—CH_2 \cdot \not\rightleftarrows C_6H_5—CH_2—\dot{C}H—CH_2—CH_3.$$

If we neglect the possibility that the small amounts formed of the isomerization products of the radical were not isolated by the author from the reaction mixture, then, as the possible cause of the high tendency of the propyl radical as compared to the 4-phenylbutyl radical to undergo isomerization, we must consider the high symmetry of the cyclic transition state (A) in the first case. The question needs further investigation.

EXPERIMENTAL

Synthesis and Decomposition of Butyryl Peroxide Labeled with C^{14} at the α-Carbon Atom

Preparation of butyryl-2-C^{14} chloride (cf. [12]). With cooling with ice water, 42 g (0.48 mole) of butyric-2-C^{14} acid* (total activity 5.2 mc) was added over a period of 1 hr with shaking to 68 g (0.57 mole) of $SOCl_2$. The reaction mixture was heated at 80° for 30 min, and the acid chloride was then distilled off. We collected a fraction of b.p. 85-105°. On refractionation we collected 41.0 g (81%) of a fraction of b.p. 100-102°; $n^{20}D$ 1.41209. The literature [16,17] gives: b.p. 100-101.5°, $n^{20}D$ 1.41209.

Preparation of butyryl peroxide labeled with C^{14} at the α-carbon atom. Butyryl peroxide labeled with C^{14} was prepared by the reaction of butyryl-2-C^{14} chloride with sodium peroxide [5]. With stirring for 1 hr, 25 g (0.32 mole) of sodium peroxide was added at 0-2° to 40 g (0.37 mole) of butyryl-2-C^{14} chloride (total activity 1.36 mc) in 200 ml of dry ether. Excess of the acid chloride was decomposed by careful addition of pieces of ice while the flask was

*Butyric-2-C^{14} acid was prepared from propyl-1-C^{14} bromide and NaCN by a previously described procedure [13]; propyl-1-C^{14} bromide was prepared from propyl-1-C^{14} alcohol [14,15].

cooled with a mixture of ice and salt. The ether layer was separated and dried with fused $CaCl_2$. Solvent was vacuum-distilled off at 15-20°, dry carbon tetrachloride (25-30 ml) was added to the residue, and the concentration of the peroxide in the CCl_4 was determined iodometrically [18]. The weight of product was 21.8 g (67%).

Decomposition of butyryl peroxide labeled with C^{14} at the α-carbon atom (cf. [5]). A solution of 60.5 g (0.35 mole) of butyryl peroxide labeled with C^{14} (total activity 1.5 mc) in 100 ml of carbon tetrachloride was added over a period of 7 hr to 250 ml of boiling dry carbon tetrachloride. The reaction mixture was boiled until a test for peroxide was negative (10-12 hr). Propyl chloride was distilled from the mixture at 45-47°. Refractionation gave 9.99 g (18%) of a fraction of b.p. 46-46.5°; $n^{18}D$ 1.3866; total activity 290 μc. The literature [19,20] gives: b.p. 46.6°, $n^{20}D$ 1.3880.

Establishment of the Position of the C^{14} in the Propyl Chloride

Hydrolysis of C^{14}-labeled propyl chloride with subsequent oxidation of the propyl alcohol to propionic acid. A 500-ml autoclave was charged with 10 g (0.13 mole) of C^{14}-labeled propyl chloride (total activity 175 μc)* and 180 ml of 10% aqueous potassium carbonate. The reaction mixture was heated with stirring for 18-20 hr at 140°. The mixture was cooled with ice water while a solution of 10.5 g (0.07 mole) of potassium permanganate in 200 ml of water was added. The mixture was left for 12 hr at 20°, the precipitate of MnO_2 was filtered off and washed with water, and the filtrate was vacuum-evaporated at 35-40° to a volume of about 40 ml and was acidified with 66% sulfuric acid. C^{14}-labeled propionic acid was extracted with ether, and the extract was dried with anhydrous sodium sulfate; solvent was distilled in a water bath; the acid distilled over at 140-141°; it amounted to 2.85 g (30%) and had $n^{15}D$ 1.3890. The literature [21, 22] gives: b.p. 140.9°, $n^{28.9}D$ 1.3859. The radioactivity of the propionic acid is given in the table (Column 1).

Distribution of Radioactivity in Reaction Products* (impulses/min · mmole)

Radioactivity of reaction products	Decomposition of butyryl-2-C^{14} peroxide in CCl_4	Oxidation of propyl-1-C^{14} alcohol	Reaction of propyl-1-C^{14} bromide with NaCN	Hydrolysis of propyl-1-C^{14} chloride	Reaction of propyl-1-C^{14} with PBr_3
	1	2	3	4	5
Butyric acid	–	–	$5 \cdot 10^3$		
Propionic acid	$18.9 \cdot 10^3$	$394 \cdot 10^3$	0.0	$89.6 \cdot 10^3$	$42.1 \cdot 10^3$
Acetic acid	$0.744 \cdot 10^3$	0.0	0.0	0.0	0.0
Methylamine	$0.732 \cdot 10^3$	–	–	–	–
Sodium carbonate	0.0	–	–	–	–
Degree of rearrangement (%)**	3.9	0.0	0.0	0.0	0.0

*The activity of propyl chloride is not given in Columns 1 and 4, that of propyl bromide is not given in Column 5, and that of the original propyl-1-C^{14} is not given in Column 2, in view of the fact that the activities of these substances were determined in the liquid state by another method (method for determining the activities of volatile liquids). For the values of these activities in absolute units, see Experimental.

**Degree of rearrangement (%) = $\frac{(\text{impulses/min} \cdot \text{mmole of } CH_3COOH) \cdot 100}{\text{impulses/min} \cdot \text{mmole of } CH_3CH_2COOH}$.

Oxidation of C^{14}-labeled propionic acid (cf. [23]). A mixture of 1 g (0.013 mole) of propionic acid obtained in the previous experiment, 12.8 g (0.043 mole) of potassium dichromate, and 120 ml of 18 N sulfuric acid was heated at 100° for 3 hr in a stream of nitrogen. Acetic acid was steam-distilled from the reaction mixture together with about 1 liter of water. The solution was made alkaline with 0.1 N NaOH (the amount of acetic acid was determined simultaneously) and vacuum-evaporated at 40-50° to about 10 ml. The residue was transferred quantitatively to a measuring flask of such volume that the sodium acetate concentration was about 10 mg/ml. The radioactivity of the acetic acid is given in the table (Column 1).

Conversion of acetic acid into methylamine by Schmidt's reaction (cf. [10]). A solution of 82 mg (0.001 mole) of sodium acetate-C^{14} in 0.5 ml of dry chloroform was cooled with ice water, and 0.5 ml of concentrated sulfuric

*6 g of the propyl chloride obtained in the decomposition of butyryl peroxide was diluted with 4 g of reagent propyl chloride.

acid was added followed at 45-55° by 2 ml of 1.3 N hydrazoic acid in chloroform. The reaction mixture was heated at 45-55° for 1-1.5 hr. The solution was cooled with ice and made alkaline with 10% aqueous sodium hydroxide; the chloroform layer was separated. From the aqueous fraction methylamine was steam-distilled into 5 ml of 5 N HCl. The solution of methylamine hydrochloride was evaporated to dryness in a vacuum, and methylamine hydrochloride was purified by repeated addition of water and evaporation. After crystallization from absolute alcohol it amounted to 42 mg; m.p. 232-233°. The literature [24] gives m.p. 232-233.5°. The results of activity measurements are given in the table (Column 1).

Fusion of sodium acetate-C^{14} with sodium hydroxide. Sodium acetate-C^{14} (200 mg; 0.0024 mole) was fused with 160 mg (0.004 mole) of sodium hydroxide until methane ceased to be liberated. The residue was transferred quantitatively to a 25-ml measuring flask, and the radioactivity of the resulting sodium carbonate was then measured. The results of the measurements are given in the table (Column 1).

Two other experiments on the decomposition of the peroxide gave agreeing results.

To prove that the butyryl peroxide was labeled with C^{14} only in the α-position and that in the reactions used for the determination of the position of C^{14} in the propyl chloride molecule no rearrangements occurred, the following experiments were carried out.

Oxidation of propyl-1-C^{14} alcohol. With ice-water cooling, to 5 g (0.083 mole) of commercial propyl-1-C^{14} alcohol (total activity 1.96 mc) and 5 g (0.047 mole) of anhydrous sodium carbonate in 20 ml of water we added a solution of 17.5 g (0.11 mole) of potassium permanganate in 400 ml of water (the temperature of the mixture was kept at not above +5°). The further treatment of the mixture was the same as in the first experiment on the establishment of the position of C^{14} in propyl chloride. The weight of propionic-1-C^{14} acid was 4.05 g (66%); $n^{15}D$ 1.3910.

The reaction conditions in the oxidation of propionic-1-C^{14} acid were the same as in the second experiment of the preceding section. The results of radioactivity measurements are given in the table (Column 2).

Oxidation of butyric-2-C^{14} acid. This was carried out under the same conditions as in the second experiment of the preceding section. The results of radioactivity measurements are given in the table (Column 3).

Preparation of known propyl-1-C^{14} chloride. Phosphorus pentachloride (105 g; 0.5 mole) was added in portions with ice-water cooling to 30 g (0.5 mole) of propyl-1-C^{14} alcohol (total activity 1.96 mc). The reaction mixture was boiled for 1 hr. Propyl-1-C^{14} chloride was distilled from the mixture at 45-50°, washed with 10 ml of water, 3 ml of concentrated sulfuric acid, and 5 ml of water, dried, and distilled at 46-47°; weight 8.8 g (23%); $n^{20}D$ 1.3880.

Hydrolysis of known propyl-1-C^{14} chloride with subsequent oxidation of propyl-1-C^{14} alcohol to propionic-1-C^{14} acid and of the latter to acetic acid. This was carried out as previously (see first and second experiments of the preceding section). The results of radioactivity measurements are given in the table (Column 4). From these results it will be seen that hydrolysis occurs without rearrangement.

Reaction of propyl-1-C^{14} alcohol with phosphorus tribromide. The reaction of propyl-1-C^{14} alcohol with PBr_3 was carried out by the previously described method [14,15]. The hydrolysis of propyl-1-C^{14} bromide with subsequent oxidation of the propyl-1-C^{14} alcohol was carried out as in the first and second experiments of the preceding section. The results are given in the table (Column 5).

Measurement of Radioactivity

Propionic and acetic acids were measured as their sodium salts, methylamine as the hydrochloride, and sodium carbonate directly. A weighed amount of the substance (or an accurately measured volume in the case of propionic acid) was dissolved in water. For the measurements on acetic acid and sodium carbonate the solutions obtained in the reactions were used: 0.1 ml of the solution was applied to a glass slide and dried at 60°, or in a vacuum desiccator (in the case of sodium carbonate). In all cases the amount of dried substance was 1 ± 0.05 mg. Radioactivity was measured in impulses/min with an end-window BFL-25 counter under constant geometric conditions.

The radioactivities of butyric-2-C^{14} acid and propyl-1-C^{14} bromide and chloride were measured by the method for the determination of the activity of volatile liquids [25].

SUMMARY

1. A study was made of the decomposition of butyryl peroxide labeled in the α-positions with radioactive C^{14} in boiling carbon tetrachloride.

2. It was shown that the propyl radical undergoes isomerization as a result of the migration of a hydrogen atom from the β-position

3. A mechanism is proposed for the isomerization examined.

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REARRANGEMENT OF THE PROPYL CATION FORMED BY THE ACTION OF NITROUS ACID ON PROPYLAMINE PERCHLORATE

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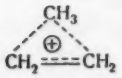
Roberts and Halmann [1] have described the rearrangement of the propyl cation:

$$CH_3—CH_2—C^{14}H_2^+ \rightleftarrows {}^+CH_2—C^{14}H_2—CH_3,$$

in the reaction of C^{14}-labeled propylamine perchlorate with nitrous acid:

$$CH_3—CH_2—C^{14}H_2—NH_2 \xrightarrow{HNO_2} CH_3—C^{14}H_2—CH_2—OH.$$

This interesting rearrangement has naturally attracted the attention of chemists because it is the simplest case of a rearrangement of the pinacolone type. This rearrangement has already found a place in the most recent organic chemistry textbooks; on the basis of this rearrangement the concept of the very simple nonclassical cation has originated:



We showed recently [2] that in carbon tetrachloride solution the free propyl radical does not undergo skeletal rearrangement. Instead, we observed isomerization with the migration of a hydrogen atom from the β-position:

$$CH_3—CH_2—C^{14}H_2^{\cdot} \rightleftarrows {}^{\cdot}CH_2—CH_2—C^{14}H_3.$$

In view of the fairly frequently observed analogy in the behavior of radicals and cations we analyzed the above-cited work of Roberts and Halmann [1] and found that their conclusion about the character of the rearrangement of the propyl cation was not the only one possible. The authors decided that the C^{14} was in the 2-position of the propyl alcohol formed ($CH_3 - C^{14}H_2 - CH_2 - OH$) on the basis of the activity of the ethylamine formed by the following reactions:

$$CH_3—CH_2—C^{14}H_2—NH_2 \cdot HClO_4 \xrightarrow{HNO_2} CH_3—CH_2—CH_2—OH \xrightarrow{KMnO_4}$$

$$\longrightarrow CH_3—CH_2—COOH \xrightarrow{HN_3} \underset{\text{active}}{CH_3—CH_2—NH_2} + CO_2.$$

The view that the radioactive C^{14} was attached to nitrogen in the ethylamine molecule was an assumption by the authors which was not proved experimentally. If, however, the C^{14} was actually in the methyl group of the ethylamine molecule, then the propyl cation did not suffer a rearrangement of the pinacolone type, but was isomerized as a result of the migration of a hydrogen anion.*

*The isomerization of a propyl cation into an isopropyl cation in the reaction of propylamine with nitrous acid was established quite a long time ago [3]; among the products of this reaction a considerable amount of isopropyl alcohol was found (yield of propyl alcohol 7%, yield of isopropyl alcohol 32%).

Contrary to the work of Roberts and Halmann, we found that under the conditions considered, the propyl cation actually underwent not skeletal rearrangement but isomerization analogous to the isomerization of the propyl radical discovered by us,* namely

$$CH_3—CH_2—C^{14}H_2^+ \rightleftarrows {}^+CH_2—CH_2—C^{14}H_3.$$

The reaction of propylamine perchlorate with nitrous acid led to the formation of propyl and isopropyl alcohols:

$$CH_3—CH_2—C^{14}H_2—NH_2 \cdot HClO_4 \xrightarrow{HNO_2} CH_3—CH_2—CH_2—OH + CH_3—CH(OH)—CH_3.$$

On oxidation of propyl alcohol with potassium permanganate we obtained propionic acid, which was oxidized further with potassium dichromate to acetic acid and carbon dioxide:

$$CH_3—CH_2—CH_2—OH \xrightarrow{KMnO_4} CH_3—CH_2—COOH \xrightarrow{K_2Cr_2O_7} CH_3—COOH + CO_2.$$

The acetic acid was subjected to: a) Schmidt cleavage, and b) alkali fission of the sodium salt. In the first case, the whole of the activity was transferred from the acetic acid to the methylamine, and in the second it was all transferred to the methane:

$$CH_3—COOH \begin{cases} \xrightarrow{HN_3} C^{14}H_3—NH_2 + CO_2 + N_2 \\ \xrightarrow{NaOH} C^{14}H_4 + Na_2CO_3 \end{cases}$$

It is therefore clear that the propyl alcohol formed in the reaction of propylamine-1-C^{14} with nitrous acid contained radioactive C^{14} only in the 1- and 3-positions. In a similar way we showed that the isopropyl alcohol also contained C^{14} in the 1- and 3-positions of the carbon chain (but not in the 2-position).

The isomerization that we found in the propyl cation is either a one-stage process of the migration of a hydrogen anion from the

$$CH_3—CH_2—C^{14}H_2^+ \rightleftarrows \left[CH_2 \begin{matrix} \diagup CH_2 \\ \diagdown C^{14}H_2 \end{matrix}\right]^+ \rightleftarrows {}^+CH_2—CH_2—C^{14}H_3 \qquad (1)$$

H

β-position of a two-stage process of the migration of a hydrogen anion from the α-position.

$$CH_3—CH_2—C^{14}H_2^+ \rightleftarrows CH_3—\overset{+}{C}H—C^{14}H_3 \text{ (a)}$$

$$CH_3—\overset{+}{C}H—C^{14}H_3 \rightleftarrows \overset{+}{C}H_2—CH_2—C^{14}H_3 \text{ (b)} \qquad (2)$$

The second mechanism is supported both by the fact that isopropyl alcohol is formed in the reaction, and by the results of the study of hydrogen exchange in paraffins (e.g. [5]). On the other hand, the literature [6] describes only the formation of isopropyl alcohol (without admixture of propyl alcohol) in the action of nitrous acid on isopropylamine.**

After we had found the rearrangement of the propyl radical [2] and that of the propyl cation, which is considered in the present paper, it was natural to check whether an analogous rearrangement is possible for an alkyl

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*In very interesting work with other amines (2-arylethylamines-1-C^{14}) [4], Roberts and co-workers proved quite definitely that skeletal rearrangements occurred in the reactions with nitrous acid.

**This work needs verification. Since the formation of propyl alcohol requires the isomerization of the more stable isopropyl cation into the less stable propyl cation ($CH_3 - \cdot \overset{+}{C}H - CH_3 \rightarrow {}^+CH_2 - CH_2 - CH_3$), it is evident that if this isomerization does go then it is only to a small extent and only very small amounts of propyl alcohol may be present in the reaction mixture.

anion. With this object we studied the carbonation of propylsodium. Propyl-1-C^{14} chloride, under the action of sodium, gave propylsodium-1-C^{14}, which on carbonation gave butyric-2-C^{14} acid exclusively:

$$CH_3-CH_2-C^{14}H_2-Cl \xrightarrow[\text{(toluene)}]{Na} CH_3-CH_2-C^{14}H_2-Na \xrightarrow[\text{(toluene)}]{CO_2}$$

$$\rightarrow CH_3-CH_2-C^{14}H_2-COOH \xrightarrow{HN_3} CH_3-CH_2-C^{14}H_2-NH_2 \xrightarrow{O}$$

$$\rightarrow CH_3-CH_2-C^{14}OOH \xrightarrow{O} \underset{\text{inactive}}{CH_3-COOH} + C^{14}O_2.$$

Hence, the propyl anion $CH_3 - CH_2 - C^{14}H_2$ does not undergo rearrangement, at least in the carbonation reaction.

EXPERIMENTAL

Synthesis of Propylamine-1-C^{14} Perchlorate

Preparation of propionitrile-1-C^{14} (cf. [1]). Diethyl sulfate (43 ml; 0.33 mole) was added dropwise at 35° to a solution of 21.6 g (0.33 mole) of $KC^{14}N$ (total activity 10 mc) in 35 ml of water and 35 ml of ethylene glycol. The mixture was left for 18 hr at 20°, and a fraction of b.p. 85-100° was then distilled off. To the distillate 15 ml of 18 N H_2SO_4 was added, and the upper layer was separated and dried over fused calcium chloride. We collected a fraction at 94-97°; weight 5.4 g (30%); total activity 3 mc. The literature [7] gives: b.p. 97-97.2°.

Hydrogenation of Propionitrile-1-C^{14} (cf. [1]). A solution of 4 g (0.07 mole) of propionitrile-1-C^{14} (total activity 1 mc)* in 15 ml of dry ether was added at 0° with stirring to 6 g (0.16 mole) of $LiAlH_4$ in 200 ml of dry ether. The mixture was stirred for 3 hr, and dropwise addition was then made of 3 ml of water and 2 ml of 20% sodium hydroxide; a further 9 ml of water was then added. From the reaction mixture propylamine-1-C^{14} was distilled into 7 ml of 70% perchloric acid; the solution was evaporated to dryness at 30-35° in a vacuum; weight 5.15 g (50%). The radioactivity is given in Table 1.

Reaction of Propylamine-1-C^{14} Perchlorate with Nitrous Acid (cf. [1])

A solution of 4.8 g (0.07 mole) of sodium nitrite in 7 ml of water was added over a period of 1 hr at 25° to a solution of 5.13 g (0.05 mole) of propylamine-1-C^{14} perchlorate in 4.5 ml of 35% perchloric acid. The reaction mixture was heated further for 1 hr at 25°. After the heating a mixture of 10 ml of propyl alcohol and 10 ml of isopropyl alcohol was added as a carrier, and 28 ml of the mixture was distilled off. The distillate was acidified with concentrated hydrochloric acid, redistilled, and then saturated with anhydrous potassium carbonate; the aqueous layer was separated, and the alcoholic layer was fractionated. Isopropyl alcohol was collected at 81-83° and propyl alcohol at 97-98.5°. The weight of the isopropyl alcohol was 10.4 g, and that of the propyl alcohol was 4.41 g. The literature [8] gives: isopropyl alcohol, b.p. 80.7-81.4°; propyl alcohol, b.p. 97.2-97.25°.

Establishment of the Position of the C^{14} in Propyl-C^{14} Alcohol

Oxidation of propyl-C^{14} alcohol. A solution of 14 g (0.09 mole) of potassium permanganate in 300 ml of water was added with ice-water cooling to 4 g (0.066 mole) of the propyl alcohol and 4 g (0.038 mole) of anhydrous sodium carbonate in 15 ml of water (the temperature of the mixture was kept at not above 5°). The mixture was left for 12 hr at 20°, and the precipitate of MnO_2 was filtered off and washed with water. The filtrate was vacuum-evaporated at 35-40° to a volume of 30-40 ml and acidified with 66% sulfuric acid. The propionic-C^{14} acid was extracted with ether; solvent was driven off on a water bath, and the acid distilled over at 140-141°; weight 2.15 g (43%); $n^{15}D$ 1.3894. The radioactivity of propionic-C^{14} acid is given in Table 1.

Oxidation of propionic-C^{14} acid (cf. [10]). A mixture of 1 g (0.013 mole) of propionic-C^{14} acid, 12.8 g (0.43 mole) of potassium dichromate, and 120 ml of 18 N H_2SO_4 was heated at 100° for 3 hr in a stream of nitrogen. From the reaction mixture acetic acid was steam-distilled off together with about 1 liter of water. The solution was made alkaline with 0.1 N NaOH (the amount of acetic acid was determined simultaneously) and vacuum-evaporated at 40-50° to about 10 ml. The residue was transferred quantitatively to a measuring flask of a volume such that the sodium acetate concentration was about 10 mg/ml. The radioactivity of the acetic acid is given in Table 1.

TABLE 1. Distribution of Radioactivity in Propyl-C^{14} Alcohol Obtained in the Reaction of Propylamine-1-C^{14} with HNO_2

Compound	Radioactivity (impulses/ min · mmole)
Propylamine-1-C^{14}	$295 \cdot 10^3$
Propionic acid	$10.9 \cdot 10^3$
Acetic acid	$0.879 \cdot 10^3$
Methylamine	$0.877 \cdot 10^3$
Sodium carbonate	0.0
Degree of rearrangement (%)*	8.0 ± 0.8

* Degree of rearrangement (%) =
$$\frac{\text{(impulses/ min · mmole of } CH_3COOH) \cdot 100}{\text{impulses/ min · mmole of } CH_3CH_2COOH}$$

TABLE 2. Distribution of Radioactivity in Butyric-C^{14} Acid Obtained in the Carbonation of Propylsodium-1-C^{14}

Compound	Radioactivity (impulses/min · mmole)
Butyric acid	$95.8 \cdot 10^3$
Propionic acid	$91.7 \cdot 10^3$
Acetic acid	0.0
Degree of rearrangement (%)	0.0

Conversion of acetic acid into methylamine by Schmidt's reaction (cf. [1]). With ice-water cooling 0.5 ml of concentrated sulfuric acid was added to 88.5 mg (0.0001 mole of sodium acetate-C^{14} in 0.5 ml of dry chloroform, and then at 45-55°, 2 ml of 1.3 N hydrazoic acid in chloroform was added. The reaction mixture was heated at 45-55° for 1-1.5 hr. The solution was cooled with ice and made alkaline with 10% aqueous sodium hydroxide; the chloroform layer was separated. Methylamine was steam-distilled from the aqueous fraction into 5 ml of 5 N HCl. The solution of methylamine hydrochloride was vacuum-evaporated to dryness; the methylamine hydrochloride was purified by repeated addition of water and evaporation. After recrystallization from absolute alcohol: weight 67.7 mg (93%); m.p. 232-233°. The literature [11] gives m.p. 232-233.5°. The results of activity measurements are given in Table 1.

Fusion of sodium acetate-C^{14} with sodium hydroxide. Sodium acetate-C^{14} (85 mg; 0.001 mole) was fused with sodium hydroxide (80 mg; 0.002 mole) until methane ceased to be liberated; the residue was dissolved in 12 ml of water, and the radioactivity of the sodium carbonate obtained was measured. The results of the measurements are given in Table 1.

Carbonation of Propylsodium-1-C^{14}

Into a three-necked flask we introduced 50 g (2.17 g-atom) of sodium, which had been previously activated with 4 ml of pentyl alcohol, together with 250 ml of dry toluene; the mixture was heated at 105° (all operations were carried out in a nitrogen atmosphere) with vigorous stirring until the metal became highly dispersed (cf. [14]). Over a period of one hour at from −3° to +7° we added 50 ml (0.55 mole) of propyl-1-C^{14} chloride* (total activity 2.5 mc) in 50 ml of dry toluene. The reaction mixture was stirred further for 1 hr at 8-19°, and then, at from −3° to −13° finely ground solid carbon dioxide was added. The excess of sodium was carefully decomposed with water, and the aqueous fraction was washed with ether; water was vacuum-distilled off down to about 50 ml. With ice-water cooling, 66% sulfuric acid was added to the residue until it reacted acid to Congo Red. Butyric-C^{14} acid was extracted with ether, the ether extract was dried with anhydrous sodium sulfate, and solvent was driven off. The acid distilled over at 163-163.5°; weight 1.55 g (3%); $n^{21}D$ 1.3989. The literature [13] gives: b.p. 163.2°, $n^{20}D$ 1.3978. The radioactivity is given in Table 2.

Establishment of the Position of the C^{14} in Butyric-C^{14} Acid

Conversion of butyric-C^{14} acid into propionic acid (cf. [14]). With ice-water cooling, to 0.88 g (0.01 mole) of butyric-C^{14} acid we added 6 ml of concentrated sulfuric acid and then 1 g (0.015 mole) of sodium azide. The mixture was stirred with a magnetic stirrer at 20° for 1 hr, then at 35° for 1 hr, and finally at 60-70° for 30 min. The solution was cooled with ice and made alkaline with 20% aqueous sodium hydroxide to a pH of 11-12. The mixture was heated for 30 min in a boiling water bath, and propylamine was driven off in a stream of nitrogen into 10 ml of 0.2 N H_2SO_4. The solution of propylamine sulfate was added to 80 ml of 5% potassium permanganate; the mixture was brought to pH 8 with 20% sodium hydroxide, and then a further 2 ml of 0.5 N NaOH was added. The mixture was heated for 30 min at 90-100°, it was acidified with sulfuric acid, and propionic acid was steam-distilled off. The solution was made alkaline with 0.1076 N NaOH (the amount of propionic-C^{14} acid was determined simultaneously) and vacuum-evaporated to dryness at 40-50°. The weight of sodium propionate-C^{14} was 0.50 g (52%).

* The propyl-1-C^{14} chloride was prepared from propyl-1-C^{14} alcohol and phosphorus pentachloride.

Oxidation of propionic-C^{14} acid. This was carried out as described above. The results of the radioactivity measurements are given in Table 2.

SUMMARY

1. In the reaction of propylamine-1-C^{14} with nitrous acid a mixture of propyl-1-C^{14} and propyl-3-C^{14} alcohols is formed.

2. The intermediately formed propyl cation does not suffer skeletal rearrangement, but is isomerized as a result of the migration of the hydride ion $CH_3 - CH_2 - C^{14}H_2^+ \rightleftharpoons {}^+CH_2 - CH_2 - C^{14}H_3$.

3. The carbonation of propylsodium-1-C^{14} was studied. It was shown that, in this reaction, the propyl anion is not isomerized.

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STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS

COMMUNICATION 9. SYNTHESIS OF O-ACETATES OF ISOMERIC DECAHYDRO-4-QUINOLINOLS AND STUDY OF THE POSSIBILITY OF O → N ACYL MIGRATION IN THE DECAHYDROQUINOLINE SERIES

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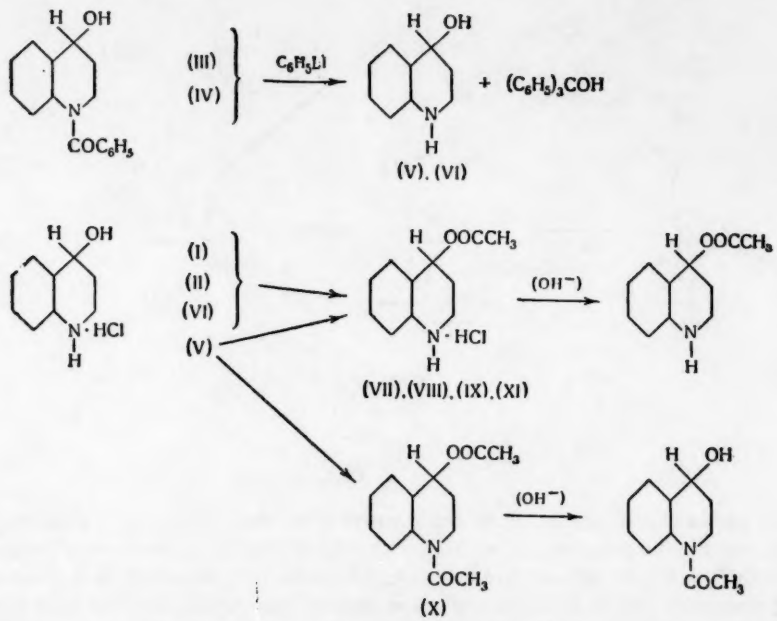
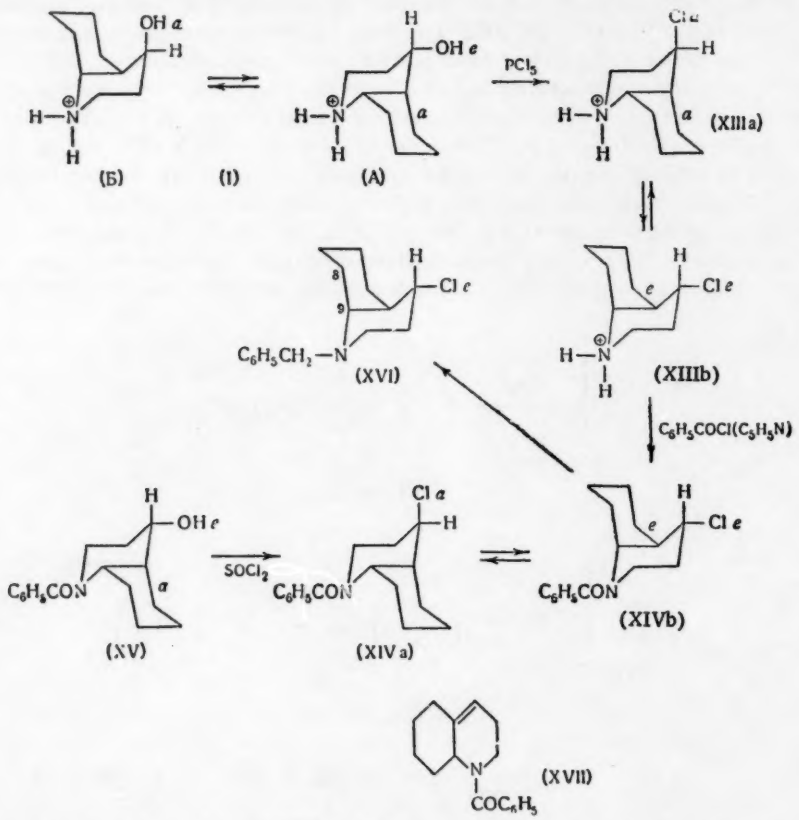
One method of establishing the steric structure of amino alcohols is the method of O → N migration of the acyl group [1,2]. It is shown in this paper that this method is unsuitable for the determination of the configuration of alcohols of the decahydro-4-quinolinol series because not one of the four isomeric O-esters of decahydro-4-quinolinol was found to be capable of isomerization into the corresponding N-acetate under the conditions used earlier for this rearrangement. In previous communications [3,4] we described the synthesis of two isomeric hydrochlorides of cis-decahydro-4-quinolinol of m.p. 275° (I) and 230° (II). Two other isomeric hydrochlorides of the trans series (V) and (VI) were obtained from the corresponding trans-1-benzoyldecahydro-4-quinolinols of m.p. 139° (III) and 222° (IV) [3]. To prevent possible isomerization in alkaline and acid hydrolysis (cf. [5]), the N-benzoyl group in the alcohols (III) and (IV) was removed by the action of an ethereal solution of phenyllithium. In this way we obtained the hydrochlorides of trans-decahydro-4-quinolinols of m.p. 199.5-201° (V) and 260.5-261.5° (VI), and the hydrochloride (VI) was found to be identical with the sample prepared earlier by a different method [4]. By short boiling of the hydrochlorides (I), (II), and (VI) with a mixture of acetic anhydride and acetyl chloride, high yields were obtained of the corresponding hydrochlorides of the O-acetates, m.p. 269-271° (VII), 248-249.5° (VIII), and 255-258° (IX). Under these conditions the hydrochloride (V) gave only the N, O-diacetate (X); the hydrochloride of the O-ester [(XI), m.p. 192-193°] was obtained by heating the hydrochloride (V) with a mixture of acetic acid and acetic anhydride.



For all the hydrochlorides of O-acetates so obtained we studied the action of alkalis under conditions which lead to rearrangement of O-esters into N-acyl derivatives in the case of O-esters of pseudotropine [1,2]. The course of the reaction was followed by chromatography on plates carrying alumina [3,11], and the structures of the reaction products were confirmed by the preparation of the picrates of the bases of the O-esters. For comparison we synthesized the N-acetyl derivatives by selective hydrolysis of the O,N-diacetyl derivatives of the decahydro-4-quinolinols, e.g. (X).

All the hydrochlorides of O-esters (VII), (VIII), (IX), and (XI), and also the O-benzoate of cis-decahydro-4-quinolinol [4], gave stable O-ester bases; hence, not one of the isomeric O-esters of decahydro-4-quinolinol was found to be capable of rearrangement into the amide. For the esters of trans-decahydroquinolinol such migration of acyl is impossible because of the rigidity of the trans-union of the bicyclic system. In the case of cis-decahydro-4-quinolinols, the close approach of the reacting groups can occur only in the conversion isomer as a double "boat" or "boat-chair." However, the stability of the free bases of O-esters of cis-decahydro-4-quinolinols shows that such a conversion cannot occur. This is indicated also by the stability of the free base of cis-4-chlorodecahydroquinoline (XII) (cf. 3-chlorotropane [6]), the hydrochloride of which (XIII) was obtained by the action of phosphorus pentachloride on the amino alcohol hydrochloride (I). The N-benzoyl derivative (XIV) was obtained by the benzoylation of the hydrochloride (XIII) with benzoyl chloride or by the action of thionyl chloride on cis-1-benzoyldecahydro-4-quinolinol of m.p. 104° (XV). The stability of the chloro derivative (XII) to reduction is characteristic: (XII) is not hydrogenated in presence of bases and is not reduced by lithium in liquid ammonia (cf. [7]) or zinc dust in acetic acid. On reduction with $LiAlH_4$, the N-benzoate (XIV) gives cis-1-benzyl-4-chlorodecahydroquinoline (XVI) in good yield.



By analogy with known examples [8,9] of the replacement of alcoholic hydroxyl by chloride which proceed as an S_N2 substitution, we may suppose that, on reaction with thionyl chloride in presence of amines or amine hydrochlorides, the alcohol (XV) or (I) will behave similarly, i.e., will react with inversion. If it is considered that the alcohols (I) and (XV) react with PCl_5 or $SOCl_2$ as conversion forms of type (a) [3], then the chloro derivatives formed may have the configurations (XIIIa) and (XIVa), which may be subsequently converted into the equatorial isomers

(XIIIb) and (XIVb). In this case, the stability of these chloro derivatives to reduction may be explained by the screening effect of the axial 8a,8-bond [10]. In the action of thionyl chloride on trans-1-benzoyldecahydro-4-quinolinol (IV), instead of the expected chloro derivative we obtained a dehydration product, which was probably 1-benzoyl-1,2,3,4,6,7,8,8a-octahydroquinoline (XVII).

EXPERIMENTAL

The chromatography was carried out on plates (13 × 18 cm) with unbound alumina (third-grade activity); the thickness of the layer was 0.5 mm [3, 11].

trans-Decahydro-4-quinolinol Hydrochloride (V). A solution of 1.28 g of trans-1-benzoyldecahydro-4-quinolinol (III), m.p. 139°, in 10 ml of tetrahydrofuran was added to a solution of phenyllithium (from 0.28 g of lithium and 2.11 ml of bromobenzene) in 12 ml of ether; the reaction mixture was boiled with stirring for 3 hr and decomposed by gradual addition of 3 ml of concentrated HCl in 10 ml of water. The aqueous layer was separated and evaporated to dryness; the residue was treated with saturated potassium carbonate solution and extracted with boiling chloroform; the extract was filtered through alumina and evaporated to dryness. The resulting crystalline product (0.74 g) was dissolved in alcohol; to the alcoholic solution of the base we added a 6.7 N solution of HCl in dioxane (1 ml), and solvent was removed in a vacuum. When the residue was ground with ethyl acetate containing a little methanol, crystallization occurred. The crystals were filtered off, washed with ethyl acetate, and dried in a vacuum. We obtained 0.51 g (54%) of trans-decahydro-4-quinolinol hydrochloride (V), m.p. 196-197°, raised by crystallization from a mixture of 2-methoxyethanol and ethyl acetate to 199.5-201°. Found: C 56.30; H 9.61; N 7.18; Cl 18.33%. $C_9H_{18}NOCl$. Calculated: C 56.4; H 9.40; N 7.31; Cl 18.5%.

trans-Decahydro-4-quinolinol Hydrochloride (VI). Rapid addition of 3.17 g of trans-1-benzoyldecahydro-4-quinolinol (IV), m.p. 222°, was made to a solution of phenyllithium prepared from 0.68 g of lithium and 5.17 ml of bromobenzene. After 1 min the reaction mixture came to the boil as a result of the heat of reaction. After treatment as in the preceding experiment, we obtained 2.16 g of the base, from which we prepared the hydrochloride by the action of 3 ml of a 4.8 N solution of HCl in dioxane on an alcoholic solution of the base. After recrystallization from alcohol and ethyl acetate, we obtained 1.82 g (78%) of trans-decahydro-4-quinolinol (VI), m.p. 260.5-261.5°, undepressed by admixture of the sample prepared earlier [4]. From the neutral part of the reaction products, after crystallization from benzene-hexane, we obtained 2.1 g (68%) of triphenylmethanol.

cis-Decahydro-4-quionolinol O-Acetate Hydrochloride (VII). A suspension of 2.92 g of cis-decahydro-4-quinolinol hydrochloride (I), m.p. 275°, in 10 ml of acetyl chloride and 10 ml of acetic anhydride was boiled for 15 min. Toward the end of this time the reaction mixture thickened because of the precipitation of crystals (after 5-7 min at the boil almost complete homogenization occurred). The crystals were transferred to a filter, washed with 30 ml of ethyl acetate, and vacuum-dried. After recrystallization from 2-methoxyethanol – ethyl acetate we obtained 2.92 g of cis-decahydro-4-quinolinol O-acetate hydrochloride (VII), m.p. 269-271° (decomp.). Found: C 56.54; H 8.62; N 6.20; Cl 15.14%. $C_{11}H_{20}NO_2Cl$. Calculated: C 56.53; H 8.57; N 6.0; Cl 15.20%.

cis-Decahydro-4-quinolinol O-Acetate Hydrochloride (VIII). A suspension of 0.40 g of cis-decahydro-4-quinolinol hydrochloride (II), m.p. 230°, in 1.5 ml of acetyl chloride and 1.5 ml of acetic anhydride was boiled under reflux. After 25 min complete dissolution occurred, and the reaction mixture then quickly thickened because of the precipitation of crystals. We obtained 0.46 g (94%) of cis-decahydro-4-quinolinol O-acetate hydrochloride (VIII), m.p. 248-249.5° (with decomposition in a sealed capillary). Found: C 56.57; H 8.67; N 6.07; Cl 15.39%. $C_{11}H_{20}NO_2Cl$. Calculated: C 56.53; H 8.57; N 6.0; Cl 15.2%.

trans-Decahydro-4-quinolinol O-Acetate Hydrochloride (IX). A mixture of 1.46 g of trans-decahydro-4-quinolinol hydrochloride (VI), m.p. 260.5-261.5°, 5 ml of acetyl chloride, and 5 ml of acetic anhydride was boiled for 1 hr 15 min. The conversion of one kind of crystals into another occurred. We obtained 1.43 g (80%) of trans-decahydro-4-quinolinol O-acetate hydrochloride (IX). After recrystallization from alcohol – ethyl acetate it had m.p. 255-258°. Found: C 56.08; H 8.41; N 6.24; Cl 15.10%. $C_{11}H_{20}NO_2Cl$. Calculated: C 56.53; H 8.57; N 6.0; Cl 15.20%.

trans-Decahydro-4-quinolinol O-Acetate Hydrochloride (XI). Acetic anhydride (1 ml) was added to a solution of 51 mg of trans-decahydro-4-quinolinol hydrochloride (V), m.p. 199.5-201°, in 1 ml of glacial acetic acid, and the mixture was heated at 40-50° for 1 hr; a further 2 ml of acetic anhydride was added, and the mixture was left overnight at 20°. On the next day heating was continued further for 2 hr at 50-55°. After this time chromatography of the reaction mixture showed the formation of appreciable amounts of the diacetate (X) (R_f in 1:1 benzene-

acetone = 0.72). Excess of reagent and solvent was vacuum-distilled off in a rotary evaporator (20 min at 40°); the residual acetic anhydride was distilled off with chlorobenzene, and the oily reaction product was rubbed out with 1 ml of ethyl acetate and 1 ml of hexane. The suspension was centrifuged; the solution was decanted from the oily residue and washed with a mixture of 1 ml of ethyl acetate and 1 ml of hexane. When this solution was allowed to stand, crystals of trans-decahydro-4-quinolinol O-acetate hydrochloride (XI), m.p. 192-193°, separated. Found: C 56.26; H 8.84; Cl 14.81%. $C_{11}H_{20}NO_2Cl$. Calculated: C 56.53; H 8.57; Cl 15.20%.

In another experiment, 0.09 g of the hydrochloride (V) was heated with 1.5 ml of acetic anhydride for 40 min at 55-57° and then, after the addition of 1 ml of acetic acid and 2.5 ml of acetic anhydride, for 2 hr further at 55 to 60°. We obtained 0.10 g (90%) of the O-acetate hydrochloride (XI).

Action of Alkalis on the Hydrochlorides of Isomeric cis-Decahydro-4-quinolinol O-Acetates. a) Potassium carbonate (2 g) was added to 0.86 g of the O-ester hydrochloride (VII), m.p. 269-271°, in 10 ml of water; the mixture was stirred for 10 min and heated on a steam bath for 10 min, and the base was extracted with chloroform. Chromatographic analysis of this extract on alumina with 3:1 acetone–methanol showed the presence of only the O-ester (R_f = 0.53). The extract was vacuum-evaporated; the residue (0.64 g) crystallized completely; m.p. 85.5-86.5°. With alcoholic picric acid this base gave a picrate, m.p. 244-245°.

b) The O-ester hydrochloride (VIII) (0.15 g), m.p. 248-249.5°, was treated as in the preceding experiment. Chromatographic analysis of the chloroform extract showed the presence of small amounts of the hydrolysis product (R_f 0.21) and the original base (R_f 0.29).

The R_f of the N-acetyl derivative is 0.90 (see below). On evaporation of the extract, the residue (0.06 g) crystallized completely. The picrate obtained from this base had m.p. 147-149° (from aqueous alcohol).

c) The O-ester hydrochloride (IX) (0.39 g), m.p. 255-258°, was treated as stated above. Chromatography of the chloroform extract showed the presence of only one spot (R_f 0.25), corresponding to the base of the original ester. The R_f of the N-acetyl derivative is 0.89 (see below). From the residue remaining after the evaporation of the chloroform extract we obtained a picrate in 80% yield; m.p. 201-204° (from alcohol).

d) To 1.4 mg of the O-ester hydrochloride (XI), m.p. 192-193°, we added 0.06 ml of 0.1 N NaOH, and the reaction mixture was heated at 100° for 10 min. Benzene was added, and the aqueous layer was saturated with potassium carbonate. Chromatography of the benzene extract gave only two spots corresponding to the hydrolysis product (R_f 0.08, average intensity) and the base of the original O-ester (R_f 0.19, very intense). The R_f of the N-acetyl derivative (see below) in the same system is 0.90.

Action of Alkalis on cis-Decahydro-4-quinolinol O-Benzoate Hydrochloride [4]. Potassium carbonate (2 g) was added to a suspension of 1.08 g of cis-decahydro-4-quinolinol O-benzoate hydrochloride, m.p. 275-277°, in 20 ml of water, and the reaction mixture was heated on a steam bath for 2 hr. The base was extracted with benzene and converted into the picrate. We obtained 1.55 g (87%) of the picrate of cis-decahydro-4-quinolinol O-benzoate, m.p. 217.5-218.5° (from alcohol). Found: C 53.86; H 4.97; N 12.04%. $C_{22}H_{24}N_4O_3$. Calculated: C 54.10; H 4.92; N 11.47%.

cis-Decahydro-4-quinolinol N,O-Diacetate and N-Acetate. a) A mixture of 0.09 g of decahydro-4-quinolinol hydrochloride (II), m.p. 230°, 0.04 g of fused sodium acetate, and 3 ml of acetic anhydride was boiled for 2 hr (internal temperature 137°). After this time, chromatographic analysis showed complete conversion of (II) into the N,O-diacetate (R_f 0.69 in 1:1 benzene–acetone). The excess of reagent was removed in a vacuum; traces of acetic anhydride were distilled off with chlorobenzene, and the dry residue was boiled with 2.5 ml of absolute methanol containing 0.1 g of KOH for 90 min (after 1 hr hydrolysis was practically complete). The reaction mixture was acidified with 0.2 ml of acetic acid and evaporated to dryness; water (about 1 ml) was added to the residue, and the reaction product was extracted with chloroform. After evaporation of the chloroform we obtained cis-1-acetyldecahydro-4-quinolinol as an oil having R_f 0.13 in 1:1 benzene–acetone.

b) To 0.62 g of base obtained from trans-decahydro-4-quinolinol hydrochloride (VI), m.p. 260.5-261.5°, in 3 ml of methanol we added 0.6 ml of acetic anhydride; the mixture was left for 15 min and then heated at the boil (5 min). Chromatographic analysis showed the presence of three components in the mixture (the starting compound and its N-mono- and N,O-di-acetates). Solvent was vacuum-evaporated off, and the residue was heated with 3 ml of pyridine and 3 ml of acetic anhydride for 3 hr. Solvent was distilled off, and the residue, which consisted of the diacetate (R_f 0.59 in 1:1 benzene–acetone), was selectively hydrolyzed as in the preceding experiment (0.65 g of

KOH in 15 ml of methanol). We obtained oily trans-1-acetyldecahydro-4-quinolinol (R_f 0.43 in 1:1 benzene–acetone).

cis-4-Chlorodecahydroquinoline Hydrochloride (XIII). We added 3.2 g of phosphorus pentachloride in one portion to a stirred suspension of 2.66 g of cis-decahydro-4-quinolinol (I), m.p. 275°. Rise in temperature with liberation of hydrogen chloride occurred. The mixture was boiled until HCl ceased to be evolved (about 15 min), and solvent was removed in a vacuum. The residue of phosphoryl chloride was distilled off with dioxane, the dry crystalline residue was dissolved in 15 ml of 96% alcohol, and 20 ml of ethyl acetate was added gradually to the solution. The hydrochloride (XIII) (1.8 g) crystallized out; m.p. 228-228.5°. Found: C 51.80; H 8.28; N 6.66; Cl 33.97%. $C_9H_{17}NCl_2$. Calculated: C 51.50; H 8.09; N 6.67; Cl 33.80%. From the mother liquors we obtained a further 0.45 g (in all 76%) of the same hydrochloride (XIII).

cis-1-Benzoyl-4-chlorodecahydroquinoline (XIV). a) With ice cooling 7.2 ml of thionyl chloride was added to 5.18 g of cis-1-benzoyldecahydro-4-quinolinol (XV), m.p. 104°, in 25 ml of dry chloroform. The reaction mixture was then boiled for 2 hr, solvent was vacuum-distilled off, and the residue was dissolved in benzene; hexane was added to the solution until a turbidity was produced. On standing, 3.05 g of cis-1-benzoyl-4-chlorodecahydroquinoline (XIV) crystallized out; after recrystallization from benzene–hexane it had m.p. 110.5-111°. Found: N 5.20; Cl 13.02%. $C_{16}H_{20}NOCl$. Calculated: N 5.05; Cl 12.80%.

b) Benzoyl chloride (1.3 ml) was added to a suspension of 2.1 g of cis-4-chlorodecahydroquinoline (XIII) in 20 ml of pyridine, and the reaction mixture was heated rapidly to 90°, when complete dissolution occurred. To the cooled reaction mixture we added 1 ml of water, and part of the pyridine was driven off in a rotary evaporator with heating to 40°; 20 ml of water was added to the residue, and the mixture was extracted with benzene. The benzene solution was vacuum-evaporated, and the residue was dissolved in 5 ml of benzene. To this solution we added warm hexane (20 ml), and crystallization set in. The crystals were filtered off, washed with hexane, and vacuum-dried. We obtained 2.28 g (82%) of cis-1-benzoyl-4-chlorodecahydroquinoline (XIV), m.p. 110.5-111°, undepressed by admixture of the sample obtained in the preceding experiment.

cis-1-Benzyl-4-chlorodecahydroquinoline (XVI). cis-1-Benzoyl-4-chlorodecahydroquinoline (XIV) (1 g) was added to a mixture of 6 ml of a 1 M ethereal solution of $LiAlH_4$ and 15 ml of tetrahydrofuran; ether was distilled off, and the reaction mixture was boiled with stirring for 3 hr. The excess of reagent was decomposed with 3 ml of ethyl acetate and then with a solution of 3 g of NaOH in 7 ml of water. The organic layer was separated, the aqueous layer was extracted with ether, and the total extract was filtered through alumina (about 2 ml) and vacuum-evaporated. The residue crystallized completely (0.9 g, m.p. about 78°). After recrystallization from hexane we obtained 0.56 g of cis-1-benzyl-4-chlorodecahydroquinoline (XVI), m.p. 82.5-83°. Found: C 73.09; H 8.46; N 5.55; Cl 13.23%. $C_{16}H_{22}NCl$. Calculated: C 72.80; H 8.36; N 5.32; Cl 13.50%.

Attempt to Reduce (XIII) and (XIV). a) Lithium (0.14 g) was added gradually to a solution of 0.42 g of cis-4-chlorodecahydroquinoline hydrochloride (XIII) in 70 ml of liquid ammonia. After 15 min the solution turned blue. The mixture was stirred for 1 hr, ammonium chloride was added, and the ammonia was evaporated. Water (10 ml) and ether were added to the residue; the aqueous layer was saturated with NaOH, and the ether layer was separated and evaporated. We obtained 0.32 g of the base of the original amine, whose picrate had m.p. 197-199°, undepressed by admixture of a known sample.

b) A mixture of 1.32 g of the hydrochloride (XIII), 3 g of zinc dust, 1.72 g of sodium acetate, and 20 ml of acetic acid was boiled with stirring for three hours. After the usual treatment we obtained 0.78 g (71%) of the base of the starting compound.

c) The hydrochloride (XIII) of the amide (XIV) were unchanged when shaken in methanol solution in a hydrogen atmosphere with PtO_2 and Pd/C in presence of sodium acetate.

1-Benzoyl-1,2,3,5,6,7,8,8a-octahydroquinoline. With ice cooling, 1.5 ml of thionyl chloride was added to 0.78 g of trans-1-benzoyldecahydro-4-quinolinol (IV), m.p. 222°, in 4 ml of chloroform. The reaction mixture was then boiled for 2 hr, and the excess of reagent and solvent was vacuum-distilled off. The residue was dissolved in hot benzene, and the solvent was filtered through alumina (about 1 ml) and evaporated. The oily residue was dissolved in hexane, and on standing there crystallized 0.46 g of 1-benzoyl-1,2,3,5,6,7,8,8a-octahydroquinoline, m.p. 77-78.5°. An analytical sample was crystallized from hexane and had m.p. 78-79°. Found: C 79.10; H 7.82; N 5.99%. $C_{16}H_{19}ON$. Calculated: C 79.60; H 7.88; N 5.81%.

SUMMARY

The O-acetates of the four isomers of decahydro-4-quinolinol were synthesized, and on the basis of the inability of these to undergo rearrangement into the corresponding N-acetates it was suggested that the method of O → N acyl migration is inapplicable in the series of decahydro-4-quinolinol derivatives.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

β-DICARBONYL COMPOUNDS

COMMUNICATION 11. REACTION OF 2-ACYLCYCLOALKANONES WITH HYDROGEN PEROXIDE

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In a previous paper [1] we showed that on treatment of 2-formylcyclohexanone [2-oxocyclohexanecarboxaldehyde] and its methyl derivatives with hydrogen peroxide in an aqueous medium there is formed a mixture of cyclopentanecarboxylic and pimelic acids. It was of interest to determine the nature of this reaction and to extend it to other 2-acylcycloalkanones.

Reaction of 2-Acylcycloalkanones with Hydrogen Peroxide

Original 2-acylcycloalkanone					Reaction products	Yield, (%)
Name	M. p., °C	B.p. in °C (p in mm)	n_D	Ref.		
2-Formylcycloheptanone	–	31-33 (0.035)	1.5110 (18°)	[3]	Cyclohexanecarboxylic and suberic acids	27 33
2-Acetylcyclohexanone	–	110-115 (20)	1.5075 (18°)	[4]	Cyclopentanecarboxylic acid and 2-methylpimelic acid (m.p. 29-50° [9])	78 20
2-Propionylcyclohexanone	–	110-116 (12)	1.5035 (20°)	[4]	Cyclopentanecarboxylic and adipic acids	59 4
2-Benzoylcyclohexanone	90-93	–	–	[5]	Cyclopentanecarboxylic and benzoic acids	30 60
2-Formyl-3,4-dihydro-1(2H)-naphthalenone	–	78-80 (0.05)	1.6350 (18°)	[6]	3-(o-Carboxyphenyl)propionic acid [10], m.p. 164-166°	80
2-Acetylcyclopentanone	–	73-75 (8)	1.4755 (18°)	[7]	Glutaric acid	58
2-(Methoxycarbonyl)-cyclopentanone	–	84-86 (3)	1.4560 (20°)	[8]	Glutaric acid	74
2-Carboxycyclohexanone	78-80	–	–	[9]	Adipic acid	85

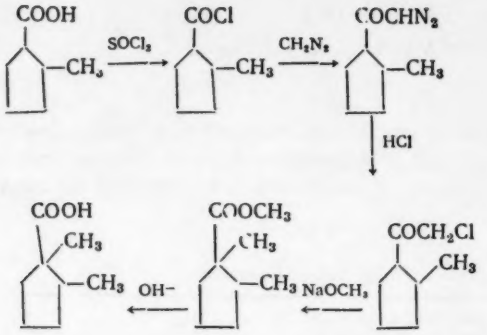
The reaction of 2-formylcyclohexanone with hydrogen peroxide is not a simple oxidation, since permanganate and chromium trioxide bring about the oxidative cleavage of this β-diketone to adipic acid. Also, the conversion of 2-formylcyclohexanone into pimelic acid does not proceed through the stage of 2-carboxycyclohexanone, inasmuch as the latter gives only adipic acid with hydrogen peroxide.

The ring contraction observed in the reaction of 2-acylcycloalkanones with hydrogen peroxide, and also the formation of 2-methylpimelic acid from 2-acetylcyclohexanone, permits us to assume that such transformations belong to the type of oxidative rearrangements. It is quite probable that these reactions have the same character as the rearrangement of acetone into propionic acid, which occurs under the action of hydrogen peroxide, selenium dioxide, and pyridine in t-butyl alcohol [2].

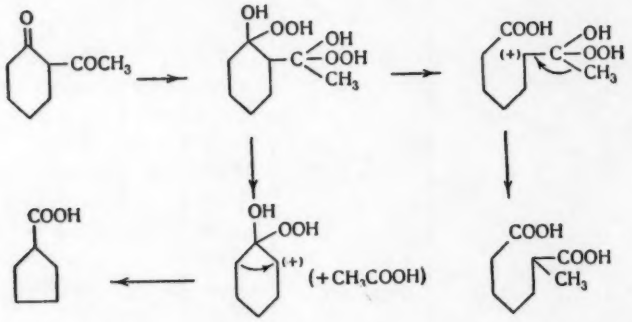
Study of the reaction of hydrogen peroxide with different 2-acylcycloalkanones (see table) showed that its course greatly depends on the structural peculiarities of the β-diketones. 2-Formylcycloheptanone and 2-acetylcyclohexanone behave like 2-formylcyclohexanone. Propionyl and benzoyl derivatives of cyclohexanone undergo ring contraction without formation of pimelic acids, but 2-formyl-3,4-dihydro-1 (2H)-naphthalenone, 2-acetylcyclopentanone, and 2-(methoxycarbonyl)cyclopentanone undergo simple oxidative cleavage to the corresponding

dicarboxylic acids. Rearrangement most readily occurs in the case of 2-formylcyclohexanone, 2-formylcycloheptanone, and 2-formyl-2,6-dimethylcyclohexanone, which react vigorously with hydrogen peroxide both in presence and in absence of alkali. The remaining 2-acylcycloalkanones, in which the carbonyl groups have a less-marked ketonic character, react with hydrogen peroxide only in an alkaline medium and reaction sometimes proceeds as simple oxidative cleavage (see last four examples in the table).

In the reaction of hydrogen peroxide with the nonenolizing 2-formyl-2,6-dimethylcyclohexanone there is formed a mixture of 1,2-dimethylcyclopentanecarboxylic acid and a dicarboxylic acid $C_6H_{12}(COOH)_2$ of unestablished structure. For the purpose of identification 1,2-dimethylcyclopentanecarboxylic acid was prepared as follows:



Under the action of hydrogen peroxide under the usual conditions the isopropyl ether of the enol form of 2-formylcyclohexanone undergoes simple oxidative cleavage to adipic acid (yield 70%). On the basis of these experiments it may be supposed that 2-acylcycloalkanones enter the oxidative rearrangement as the diketo forms, probably through the stage of unstable peroxy compounds:



In accordance with well-known views on the mechanism of the decomposition of hydroperoxides of monoketones [11], the decomposition of diperoxy compounds of 2-acylcycloalkanones may be represented as a process including the heterolytic rupture of bonds and the rearrangement of cations.

EXPERIMENTAL

Reaction of 2-Acylcycloalkanones with Hydrogen Peroxide. The reaction was carried out by the previously described method with the use of 3 M NaOH or KOH. The oxidation of 2-(methoxycarbonyl)cyclopentanone was carried out under more severe conditions (6 M alkali, 100°, 90 min). In the case of 2-formyl-3,4-dihydro-1 (2H)-naphthalenone a higher yield of reaction product was obtained when caustic alkali was replaced by an equivalent amount of sodium carbonate.

Reaction of 2-Formyl-2,6-dimethylcyclohexanone with Hydrogen Peroxide. To 2 g of 2-formyl-2,6-dimethylcyclohexanone [b.p. 56-59°] [12] in 5 ml of water we added 11 ml of 28% hydrogen peroxide. At the end of the exothermic reaction the oil formed was extracted with ether and vacuum-fractionated. We obtained 1 g (50%) of 1,2-dimethylcyclopentanecarboxylic acid; b.p. 83-85° (2 mm), $n^{18}D$ 1.4485. Found: C 67.02, 67.17; H 9.91, 9.72%.

$C_8H_{14}O_2$. Calculated: C 67.57; H 9.93%. The amide had m.p. 88-89° (from heptane). Found: C 67.93, 67.68; H 10.55, 10.65; N 9.83, 9.64%. $C_8H_{15}ON$. Calculated: C 68.04; H 10.70; N 9.92%.

We isolated also 0.7 g (29%) of a dicarboxylic acid of unestablished structure, b.p. 173-175° (2 mm) and m.p. 42-43°. Found: C 54.83, 54.77; H 7.75, 7.74. $C_8H_{14}O_4$. Calculated: C 55.16; H 8.10%. The titration equivalent found was 93.8, 94; the calculated value was 94.

Reaction of 2-(Isopropoxymethylene)cyclohexanone with Hydrogen Peroxide. With stirring, 15 ml of 28% hydrogen peroxide was added to 3 g of 2-(isopropoxymethylene)cyclohexanone [b.p. 78-80° (1 mm), $n^{20}D$ 1.4942] [13] and 3.8 g of sodium carbonate in 20 ml of water. The mixture was left for 1 hr at room temperature, and ether then extracted 1.8 g (70%) of adipic acid.

Oxidation of 2-Formylcyclohexanone with Potassium Permanganate. A 2% solution of potassium permanganate was added in portions with stirring to a mixture of 3 g of 2-formylcyclohexanone and 3 g of sodium carbonate in 20 ml of water until a stable (lasting about 5 min) red coloration appeared. The excess of permanganate was destroyed by the addition of sodium bisulfite. After filtration the solution was evaporated to dryness. From the residue acetone extracted 2.7 g (77%) of adipic acid.

Oxidation of 2-Formylcyclohexanone with Chromium Trioxide. A solution of 20 g of chromium trioxide in 100 ml of 70% acetic acid was added to 3 g of 2-formylcyclohexanone in 20 ml of acetic acid, and the reaction mixture was left for 12 hr at room temperature. The excess of chromium trioxide was destroyed by the addition of methanol, and the solution was evaporated to dryness. From the residue acetone extracted 1.1 g (31%) of adipic acid.

Preparation of Chloromethyl 2-Methylcyclopentyl Ketone. Chloromethyl 2-methylcyclopentyl ketone was prepared by the action of diazomethane on 2-methylcyclopentanecarbonyl chloride (b.p. 171-172°) [14] by Mousseron's method [15], as described for chloromethyl cyclohexyl ketone; yield 60%; b.p. 85-86° (15 mm), $n^{18}D$ 1.4715. Found: C 59.41, 59.42; H 8.07, 7.90; Cl 22.19, 22.21%. $C_8H_{13}ClO$. Calculated: C 59.81; H 8.09; Cl 22.12%.

Conversion of Chloromethyl 2-Methylcyclopentyl Ketone into 1,2-Dimethylcyclopentanecarboxylic Acid. On treatment of chloromethyl 2-methylcyclopentyl ketone with methanolic sodium methoxide by Mousseron's method [15], we obtained 1,2-dimethylcyclopentanecarboxylic acid in 25% yield; b.p. 83-85° (2 mm); $n^{19}D$ 1.4495. The amide had m.p. 83-84° (from heptane). This amide gave no depression of melting point in admixture with the amide of 1,2-dimethylcyclopentanecarboxylic acid isolated in the reaction of 2-formyl-2,6-dimethylcyclohexanone with hydrogen peroxide.

SUMMARY

Depending on the structure of the β-diketone, reaction of a 2-acylcycloalkanone with hydrogen peroxide may proceed with oxidative cleavage or with oxidative rearrangement accompanied by ring contraction and formation of dicarboxylic acids.

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TRANSFORMATIONS OF BUTYLPHENOLS OVER DEHYDROCYCLIZATION CATALYSTS

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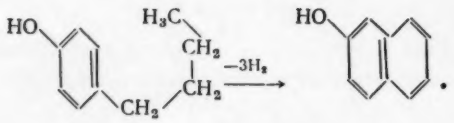
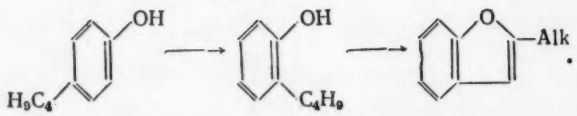
Insufficient study has been devoted to the behavior of alkylphenols under dehydrocyclization conditions. Hansch [1] and Corson [2] found that, when passed as vapor over Pt – C, Pd – C, Cr – C, and Cr – Cu – C, o-alkylphenols are converted into alkylbenzofurans; the latter are obtained in fairly good yields when chromic oxide on alumina is used as catalyst and the alkylphenols are diluted with water [2]. In view of this it was considered to be of interest to study the behavior of butylphenols under dehydrocyclization conditions.

In the present work we investigated the transformations of o- and p-butylphenols, 6-butyl-m-cresol, and 4-butyl-o-cresol in presence of platinized charcoal, chromic oxide on alumina, and also on magnesia, and chromic and potassium oxides on alumina at temperatures in the range 350-550°. Rise in temperature, and also reduction in space velocity, lowered the yields of catalyzates as a result of partial cracking of the side group, resinification, and carbon formation on the catalyst.

Investigation of the phenolic part of the catalyzates showed that, in all experiments, it contained, in addition to unchanged butylphenol, products of the cracking of the butyl group of the original phenol. Maximum cracking was observed when catalysts containing alumina were used. From the neutral part of the catalyzate obtained in the investigation of o-butylphenol over a Cr_2O_3 – MgO catalyst at 520° we isolated only ethylbenzofuran (yield about 2%) and a mixture of benzofuran and methylbenzofuran (yield 2.5%), the presence of which was confirmed spectroscopically. From the acidic part of the products of the transformation of p-butylphenol under the same conditions, apart from cracking products, we isolated 2% of 2-naphthol:



From the neutral part of the catalyzates we isolated a mixture of benzofurans in very low yield. The formation of these under these conditions may be explained only on the assumption of the partial isomerization of p- into o-butylphenol with subsequent cyclization:



In the investigation of the transformations of 6-butyl-m-cresol over Cr_2O_3 – MgO at 550° we observed the formation of 6-methylbenzofuran:

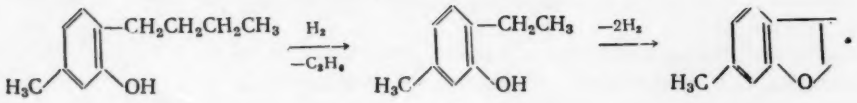
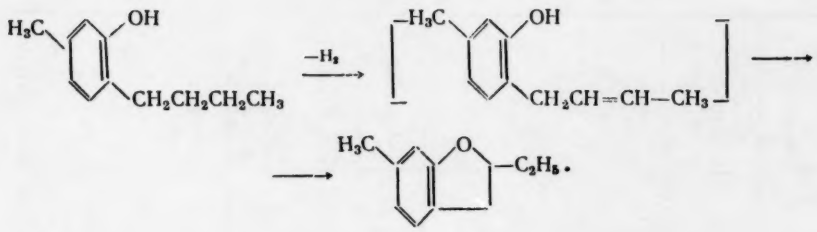


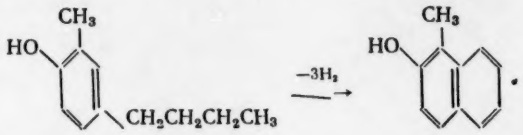
TABLE 1.

Substance	B.p. in °C (p in mm)	M. p., (°C)	$n^{20}D$	d^{20}_4	M. p. of phenoxy derivative (°C)
o-Butyrylphenol	128-130 (18)	–	1.5400	1.0681	–
p-Butyrylphenol	–	90-91	–	–	–
6-Butyryl-m-cresol	136-138 (8)	15-17	1.5406	1.0501	(m.p. of oxime, 74°)
4-Butyryl-o-cresol	188-190 (9)	131-132	–	–	–
o-Butylphenol	110-122 (17)	–	1.5212	0.9743	104-105.6
p-Butylphenol	132-135 (15)	–	1.5170	0.9717	79.7-80.7
6-Butyl-m-cresol	115-116 (5)	17-18	1.5185	0.9645	83.5-84.0
4-Butyl-o-cresol	118-120 (5)	23-23	–	–	–

It was of interest to find that over platinized charcoal at 350-400°, 6-butyl-m-cresol gave 2-ethyl-2,3-dihydro-6-methylbenzofuran:



Investigation of the transformations of 4-butyl-o-cresol over a chromia-magnesia catalyst at 480-550° showed that the phenolic part of the catalyzate contained only about 1% of 1-methyl-2-naphthol.



Hence, under our conditions, butylphenols mainly undergo cracking of the butyl group. In addition, cyclization occurs, mainly at the oxygen with formation of substituted benzofurans; but to a small extent dehydrocyclization occurs with formation of the corresponding naphthols.

EXPERIMENTAL

All the butylphenols were synthesized by reducing the corresponding butyrylphenols prepared by the acylation of the phenols with butyryl chloride. The reduction was carried out by the Clemmensen method [3] with amalgamated zinc in hydrochloric acid. Table 1 gives the properties of the ketones and butylphenols obtained. The butylphenols were characterized as phenoxy derivatives.

The chromic oxide (20%) on magnesia catalyst was prepared by two methods: a) impregnation of magnesium oxide with chromium nitrate solution with subsequent thermal decomposition of the latter; b) precipitation of the hydroxides from a mixed solution of the nitrates with ammonia. By the second method we prepared also the chromic oxide on alumina catalyst. The alumina – chromia – potassia catalyst was prepared by the impregnation of aluminum oxide with solutions of chromic acid and potassium carbonate [4].

Platinized charcoal (10% Pt) was prepared by the impregnation of activated birch charcoal with a solution of chloroplatinic acid with subsequent reductive decomposition of the latter in a stream of hydrogen with gradual rise in temperature to 350°. All experiments were carried out in a flow apparatus with automatic feed of the phenols. To separate the phenolic part from the catalyzates, these were treated with 10% sodium hydroxide solution. After isolation by acidification and drying, the phenolic and neutral parts of the catalyzates were fractionated under

TABLE 2. Results of Experiments on the Catalytic Transformations of p-Butylphenol

Experiment	Amount of p-butylphenol passed (g)	Catalyst	Temp., °C	Space velocity (hr^{-1})	Yield of catalyzate (% on butylphenol passed	Comp. of catalyzate (% of catalyzate)			Resinous residue (% on catalyzate)
						phenolic part	neutral part	2-naphthol	
1	39,4	Cr_2O_3 — MgO	500	0,15	78,9	77,0	4,5	0,9	17,6
2	24,5	Cr_2O_3 — MgO	510	0,12	72,6	71,8	6,1	1,3	20,8
3	18,8	Cr_2O_3 — MgO	550	0,14	67,7	58,4	8,2	1,3	32,1
4	21,8	V_2O_5, Cr_2O_3, MgO	500	0,14	79,7	38,2	34,9	Следы	26,9
5	23,9	Pt — C	400	0,12	83,7	64,8	6,8	—	28,4
6	73,6	Cr_2O_3 — Al_2O_3	475	0,21	44,8	31,1	27,7	—	41,9

TABLE 3. Results of the Catalytic Transformations of 6-Butyl-m-cresol

Experiment	Amount of 6-butyl-m-cresol passed (g)	Catalyst	Temp., °C	Space velocity (hr^{-1})	Yield of catalyzate (%) on alkylphenol passed	Comp. of catalyzate (% on original alkylphenol)		Resinous residue and losses (% on original alkylphenol)
						phenolic part	neutral part	
7	50	Cr_2O_3 — MgO *	410	0,2	87,0	78,2	8,8	13
8	43	Cr_2O_3 — MgO	450	0,2	84,0	75,7	8,3	16
9	45	Cr_2O_3 — MgO	490	0,2	80,0	75,5	4,5	20
10	50	Cr_2O_3 — Al_2O_3	475	0,2	86,0	72,0	14,0	14
11	50	Cr_2O_3 — Al_2O_3	520	0,2	78,0	62,4	15,4	22,2
12	100	Cr_2O_3 — MgO	550	0,2	62,0	46,0	16,0	38
13	70	K_2O, Cr_2O_3 — Al_2O_3	550	0,15	50,0	35,0	15,0	50
14	28	Pt — C	350	0,2	92,3	81,4	10,9	7,7
15	25	Pt — C	400	0,2	92,0	69,2	22,8	8,0
16	25	Pt — C	400	0,1	88,0	61,6	26,4	12,0

*Prepared by the impregnation method.

reduced pressure. 2-Butylphenol was passed in 25-ml portions through a layer of fresh chromia-magnesia catalyst at 520° in a feeble stream of nitrogen with a space velocity of 0.17 hr^{-1}. The yield of catalyzate was 82%. Apart from nitrogen, the gas collected contained 30% of olefins, 32% of hydrogen, and 7% of saturated hydrocarbons. The liquid catalyzate consisted of 67% of phenolic part and 33% of neutral part. From the phenolic part we isolated phenol, o-cresol, and unchanged o-butylphenol. From the neutral part of the catalyzate we isolated three fractions:

Fraction I: b.p. 78-92° (20 mm), $n^{20}D$ 1.5552; λ_{max} 242 mμ; log ε 3.99; λ_{max} 275 mμ; log ε 3.29; λ_{max} 282 mμ; log ε 3.26. Yield 1.2% on the catalyzate. For benzofuran the literature [5] gives: b.p. 67.5° (20 mm), $n^{25}D$ 1.5635; λ_{max} 244 mμ; log ε 4.03; λ_{max} 274 mμ; log ε 3.39; λ_{max} 281 mμ; log ε 3.42.

Fraction II: b.p. 92-101.3° (20 mm), $n^{20}D$ 1.5489; d^{20}_4 1.0259; λ_{max} 245 mμ; log ε 3.97; λ_{max} 275 mμ; log ε 3.36; λ_{max} 282 mμ; log ε 3.35. Yield 1.1% on the catalyzate. For methylbenzofuran the literature [6] gives: b.p. 192° (744 mm), $n^{25}D$ 1.5460; d^{20}_4 1.0424; λ_{max} 246 mμ; log ε 4.09; λ_{max} 276 mμ; log ε 3.51; λ_{max} 383 mμ; log ε 3.51.

Fraction III: b.p. 101.3-103.8° (20 mm), $n^{20}D$ 1.5518; d^{20}_4 1.0218. Yield 1.8% on the catalyzate. For ethylbenzofuran the literature [6] gives: b.p. 99-100° (19 mm), d^{20}_{20} 1.0196; $n^{26}D$ 1.5522.

Table 2 gives the results of experiments on the investigation of the transformations of p-butylphenol in presence of various catalysts. The phenolic part of the catalyzates consisted of a mixture of substituted phenols, in which we succeeded in identifying by the melting points of their phenoxy [presumably O-phenyl is meant — Publisher] derivatives: phenol, p-cresol, p-ethylphenol, and unchanged p-butylphenol. The neutral parts of the

catalyzates consisted of mixtures of alkylbenzofurans, which were identified by their ultraviolet absorption spectra. Also, in the neutral part of the catalyzate from Expt. 6 we succeeded in identifying naphthalene from the melting point of the picrate (148-149°).

Table 3 gives the results of experiments on the transformations of 6-butyl-m-cresol in presence of various catalysts. From the melting points of their phenoxy derivatives we identified the following in the phenolic part of the catalyzate: phenol, m-cresol, 2,5-xylenol, and unchanged 6-butyl-m-cresol. In the neutral parts of the catalyzates, from Experiments 9, 10, 11, and 13, we succeeded in identifying 2-methylnaphthalene by the melting point of its picrate (115-116°). In Expt. 13 the amount of 2-methylnaphthalene was about 1%. Also, from the neutral part of the catalyzate from Expt. 12 we isolated 6.4% of 6-methylbenzofuran with the following properties: b.p. 82-85° (12 mm), $n^{20}D$ 1.5490 and d^{20}_4 1.0440; m.p. of picrate 64-65.5°. For the picrate of 6-methylbenzofuran the literature [7] gives m.p. 67°. From the neutral parts of the catalyzates obtained in Expts. 15 and 16, we isolated 2.2% and 4.0%, respectively, of 2-ethyl-2,3-dihydro-6-methylbenzofuran, b.p. 115.5-116° (20 mm), $n^{20}D$ 1.5250 and d^{20}_4 0.9797.

4-Butyl-o-cresol was passed through a layer of chromia–magnesia catalyst at a space velocity of 0.15 hr^{-1} at 480° and 550°. The yields of catalyzates were 73.3% and 66.6%, respectively. In view of their extremely small amounts, the neutral parts of the catalyzates were not investigated. In the phenolic part we identified o-cresol, 2,4-xylenol, and unchanged 4-butyl-o-cresol. Also, we isolated about 1% of 1-methyl-2-naphthol (experiment at 480°), which was identified by the melting point of the picrate (163-164°). For the picrate the literature [8] gives m.p. 163-164°.

SUMMARY

1. An investigation was made of the transformations of the isomeric butylphenols and butylcresols over dehydrocyclization catalysts under atmospheric pressure at 350-550° in a flow system.

2. Under the given conditions the main reaction was the partial cracking of the butyl group with formation of lower phenols.

3. Of the two possible courses of the dehydrocyclization reaction there is a predominance of ring closing of the side alkyl group at oxygen with formation of substituted benzofurans. There is simultaneous dehydrocyclization with formation of the corresponding naphthols, but the yields of these do not exceed 2%.

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CATALYTIC TRANSFORMATIONS OF 1-METHYLCYCLOHEXENE

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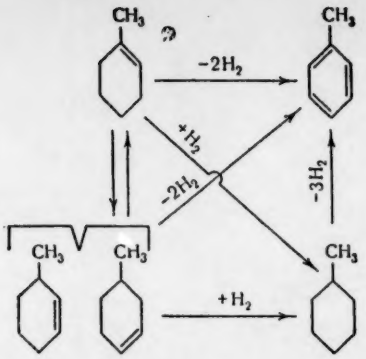
There is already much information in the literature [1-6] on the catalytic transformations of cyclohexenes, particularly 1-methylcyclohexene, in presence of various metal oxides, and also aluminum silicates. In some of the papers [1,2,4] various views are advanced on the mechanism of the catalytic transformations of hydrocarbons of this class. Zelinskii and Arbuzov [1,2] showed that in presence of alumina and silica gel at 400-450°, 4-methylcyclohexene is isomerized into dimethylcyclopentene. Later, Adkins and Roebuck [3] studied the transformations of 1-methylcyclohexene in contact with pure alumina at 470-480°, and showed that this hydrocarbon is isomerized into 2,3-dimethylcyclopentene and 3-ethylcyclopentene. Under the action of alumina these are further transformed into 1,2-dimethyl- and 1-ethyl-cyclopentenes, respectively. Rachinskii and Rzhekhina [6] found that the main products of the transformations of 1-methylcyclohexene under the action of granulated gumbrin at 320° are dimethylcyclopentene, ethylcyclopentene, and ethylcyclopentane. The authors proved the presence of these hydrocarbons by the physical constants of the appropriate catalyzate fractions, which were hydrogenated and sulfonated. Toluene was also detected in the reaction products spectroscopically. In the opinion of the authors, the catalytic transformations of 1-methylcyclohexene under the given conditions are accompanied by partial destructive decomposition, as a result of which cyclohexene and its isomerization products are formed. Petrov and co-authors [4,5] studied the behavior of cycloalkenes, in particular 1-methylcyclohexene, at 250° in presence of a Houdry aluminum silicate catalyst. The authors report that under their conditions 1-methylcyclohexene suffered scarcely any isomeric changes. In this case, the main reaction product was methylcyclohexane (80%).

We were interested to find conditions under which it would be possible to effect the displacement of the double bond in the six-membered ring from the 1,2- to the 2,3- or 3,4-position with the object of obtaining 3- or 4-methylcyclohexene. These isomers can serve as raw material for the synthesis of 2- or 3-methyladipic acid by oxidation at the double bond of the ring. With this object we studied the transformations of 1-methylcyclohexene in presence of various catalysts: activated birch charcoal containing 5% of barium chloride, a catalyst consisting of 10% Fe_2O_3, and 90% Al_2O_3, and activated gumbrin at temperatures in a wide range (250-450°). We studied also the transformations of 1-methylcyclohexene and 4-methylcyclohexene in contact with an aluminum oxide – ferric oxide catalyst at 400° and 180 mm with one and two passages over the catalyst. The results of our investigation showed that in the range 250-300° in presence of activated birch charcoal containing 5% of barium chloride, 1-methylcyclohexene suffers no appreciable change. The main products of the transformations of 1-methylcyclohexene in presence of gumbrin at 300° are methylcyclohexane (60%) and 4-methylcyclohexene (14%). Investigation of the products of the transformation of 1-methylcyclohexene in presence of an alumina – ferric oxide catalyst in the range 250-450° showed that they consist of 4-methylcyclohexene, methylcyclohexane, toluene, and unchanged 1-methylcyclohexene. The possibility is not excluded that some 3-methylcyclohexene was also present in the catalyzates.

From our results on the products of the transformations, we may conclude that the main reactions occurring under the given conditions are the isomerization of the double bond in the six-membered ring, the dehydrogenation of methylcyclohexenes (the original and the 4-methylcyclohexene formed) and methylcyclohexane into toluene, and probably also redistribution of hydrogen with formation of methylcyclohexane and toluene. The transformations of these hydrocarbons may be represented as shown on the following page.

Investigation of the Raman spectra of the hydrogenated transformation products showed the absence of cyclopentanes among them.



EXPERIMENTAL*

Original Hydrocarbons. 1-Methylcyclohexene [7] was prepared in 42% yield by the dehydrochlorination of a mixture of isomeric chloromethylcyclohexanes in presence of activated birch charcoal containing 5% of barium chloride at 220°. 1-Methylcyclohexene was isolated from the mixture of isomeric methylcyclohexenes by careful fractionation through a column of 24-plate efficiency; it had b.p. 108-109° (748 mm), $n^{20}D$ 1.4505, and d^{20}_4 0.8088.

TABLE 1. Results of the Catalytic Transformations of 1-Methylcyclohexene in Presence of Fe_2O_3 (10%) – Al_2O_3

Temp., °C	Pressure (mm)	Composition of catalyzate (%)			
250	Atmospheric	79,3	15,6	1,9	3,2
250	180	86,1	3,8	0,3	9,8
300	Atmospheric	28,2	24,3	8,8	38,7
300	180	71,2	7,9	1,4	19,5
400	Atmospheric	12,3	11,0	15,4	61,3
400	180	49,7	17,0	2,0	31,3
450	Atmospheric	8.8	7,8	10,5	72,9
450	180	23,5	10,8	1,5	64,1

4-Methylcyclohexene was prepared by the dehydrochlorination of the product of the reaction of 4-methylcyclohexanol with concentrated hydrochloric acid; it had b.p. 100-100.8° (742 mm), $n^{20}D$ 1.4420, and d^{20}_4 0.7999. The purities of these hydrocarbons were checked by chromatography. Methylcyclohexane, after purification over silica gel, had b.p. 100.5° (750 mm), $n^{20}D$ 1.4232, and d^{20}_4 0.7693. Toluene had b.p. 110.6° (760 mm), $n^{20}D$ 1.4965, and d^{20}_4 0.8670.

Catalysts. Alumina – ferric oxide catalyst (Al_2O_3 + 10%Fe_2O_3)was prepared by the coprecipitation of molar solutions of ferric and aluminum nitrates with 12% ammonia solution at room temperature with mechanical stirring. The combined precipitate of hydroxides was washed with distilled water to effect the complete removal of nitrate ions. Gumbrin (natural aluminum silicate of the Georgian SSR) was activated by treatment with 10% hydrochloric acid and heating for 4 hr, after which it was washed with distilled water until chloride ions had disappeared. The dried precipitate of hydroxides was then tableted in the form of cylinders, 4 mm both in height and in diameter. Barium chloride on charcoal was prepared by the impregnation of activated birch charcoal with the calculated amount of barium chloride solution.

Isomerization of 1-Methylcyclohexene. The experiments were carried out in the usual laboratory flow apparatus at atmospheric and at reduced pressures. The space velocity of the feed of the hydrocarbon was 0.2 hr^{-1}. In experiments with Fe_2O_3 – Al_2O_3 the yield of liquid catalyzate with boiling limits of 99-110° was about 90%. The

*Z. P. Polyakova took part in the experimental work.

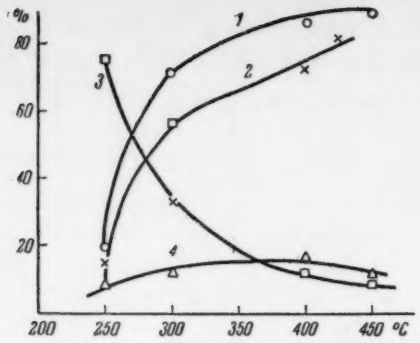


Fig. 1. Temperature-dependence of the composition of the catalyzate obtained in experiments at atmospheric pressure: 1) 1-methylcyclohexene (% in catalyzate); 2) toluene; 3) 4-methylcyclohexene; 4) methylcyclohexane.

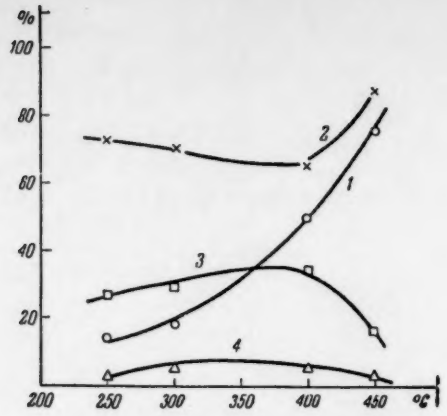


Fig. 2. Temperature-dependence of the composition of the catalyzate obtained in experiments at 180 mm: 1) 1-methylcyclohexene; 2) toluene; 3) 4-methylcyclohexene; 4) methylcyclohexane.

TABLE 2. Transformation of Hydrocarbons in Contact with Fe_2O_3 (10%) – Al_2O_3 at 400° and 180 mm

Original hydrocarbon	Composition of catalyzate (%)			
1-Methylcyclohexene	49,7	17,0	2,0	31,3
Catalyzate from Expt. 1	18,9	12,5	2,2	66,4
4-Methylcyclohexene	25,5	25,4	9,1	40,0
Catalyzate from Expt. 3*	12,0	7,5	8,6	64,3
Methylcyclohexane	—	—	91,5	5,2
Toluene	—	—	—	99,0

*Judging from the results of chromatographic analysis, this catalyzate probably contains also 7.6% of 3-methylcyclohexene.

amount of gas liberated was extremely small. At 400° and atmospheric pressure the gas consisted mainly of hydrogen and contained 1-3% of methane. The catalyzates were analyzed by the method of gas–liquid chromatography in a two-meter column filled with diatomite impregnated with tritolyl phosphate (20%). As carrier gas we used hydrogen, which was passed through the column at a rate of 40 ml/hr. The results of the catalytic transformations of 1-methylcyclohexene are given in Table 1 and 2. The temperature-dependence of the contents of hydrocarbons in the catalyzate, calculated on the 1-methylcyclohexene converted, at atmospheric and at reduces pressures is shown in Figs. 1 and 2.

It will be seen from Table 1 that in presence of an alumina – ferric oxide catalyst at 250-450° and atmospheric pressure 1-methylcyclohexene is preferentially isomerized into 4-methylcyclohexene and dehydrogenated into toluene. The formation of some methylcyclohexane under the given conditions probably occurs as a result of hydrogen redistribution. The largest amount of 4-methylcyclohexene is formed at 300°. With rise in temperature the content of 4-methylcyclohexene in the catalyzate falls and the amount of toluene rises. At the same time, the degree of conversion of the 1-methylcyclohexene increases. At reduced pressure the optimum temperature for the isomerization of 1-methylcyclohexene into 4-methylcyclohexene is 400°. Here again, with rise in temperature the extent of the isomerization falls and the yield of toluene rises. The difference in the courses of the temperature curves for the transformations of 1-methylcyclohexene at atmospheric and at reduced pressures is probably to be explained by the difference in the time of contact of the original hydrocarbon and the catalyst.

We considered it to be of interest also to elucidate the transformations of 1-methylcyclohexene in presence of an alumina – ferric oxide catalyst at 400° and 180 mm. With this object we investigated the transformations of 4-methylcyclohexene, methylcyclohexane, and toluene. The results are presented in Table 2.

It will be seen from Table 2 that, as a result of two passages of 1-methylcyclohexene, the amount of toluene formed is almost doubled (as compared with one passage), and the yield of 4-methylcyclohexene is reduced to 12.5%. The conversion of the original hydrocarbon rises to 81.1%. The main products of the transformations of 4-methylcyclohexene are 1-methylcyclohexene (25.5%), methylcyclohexane (9.1%), and toluene (40%). In a second passage of the transformation products of 4-methylcyclohexene in presence of $Fe_2O_3 - Al_2O_3$ at 400° it was found that its conversion rises to 92.5% and the toluene content of the catalyzate rises to 64.3%. In addition, there is a fall in the yield of 1-methylcyclohexene to 12%. The methylcyclohexane content of the catalyzate remains almost unchanged. Moreover, by gas–liquid chromatography on this catalyzate we found 3-methylcyclohexene (7.6%). The treatment of methylcyclohexane under the same conditions gave a catalyzate containing 5.2% of toluene. Under the same conditions the latter undergoes scarcely any change.

On analysis of the data in Table 2 it is seen that in the repassage of the products of the transformations of 1- and 4-methylcyclohexenes over the catalyst transformations occur in all four hydrocarbons composing the first catalyzates. As in the first passages, the main reactions are displacement of the double bond in methylcyclohexenes, their dehydrogenation, and redistribution of hydrogen. Hence, increase in the amount of toluene in the catalyzates obtained in the second passage occurs both as a result of transformations of the original methylcyclohexenes and as a result of their isomerization. Also, toluene is formed by the dehydrogenation of methylcyclohexane. The formation of methylcyclohexane is probably a result of redistribution of hydrogen in the original methylcyclohexenes.

SUMMARY

1. The transformations of 1- and 4-methylcyclohexenes in presence of an alumina – ferric oxide catalyst were investigated.

2. In the range 250-450° in presence of this catalyst, the main transformations of 1- and 4-methylcyclohexenes were isomerization with displacement of the double bond, dehydrogenation into toluene, and redistribution of hydrogen with formation of methylcyclohexane and toluene.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES OF TARTARY PETROLEUMS

COMMUNICATION 7. GASOLINE FROM PETROLEUM OF THE SHUGUROV DEPOSITS

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In previous papers [1] we have reported on the composition of gasolines in deposits associated with the Devonian and carboniferous systems in which the collectors were sandy rocks. In the present investigation we studied the composition of the gasoline separated from Shugurov petroleum (bore hole 10) associated with the carboniferous system, in which the collector was formed by carbonate rocks.

TABLE 1.

Name of hydrocarbon	Content (% by wt. on gasoline)	Name of hydrocarbon	Content (% by wt. on gasoline)
Paraffins			
Gaseous hydrocarbons	0.55	2,5-Dimethylhexane	0.26
2-Methylbutane	4.53	3-Ethylhexane	0.37
Pentane	10.15	2-Methylheptane	2.40
2,2-Dimethylbutane	0.27	3-Methylheptane	0.72
2,3-Dimethylbutane	1.28	4-Methylheptane	1.56
2-Methylpentane	3.59	Octane	8.23
3-Methylpentane	2.39	2,3,5-Trimethylhexane	0.29
Hexane	5.55	3,4,5-Trimethylhexane	0.29
2,2-Dimethylpentane	0.13	2,2-Dimethylheptane	0.57
2,3-Dimethylpentane	0.42	2,6-Dimethylheptane	2.02
2,4-Dimethylpentane	0.13	4,4-Dimethylheptane	0.37
2-Methylhexane	1.47	4-Ethylheptane	0.35
3-Methylhexane	3.08	2-Methyloctane	0.79
3-Ethylpentane	0.75	3-Methyloctane	1.30
Heptane	7.30	4-Methyloctane	1.04
2,3-Dimethylhexane	0.50	Nonane	2.82
2,4-Dimethylhexane	1.03		
		Total	66.50
Cyclopentanes			
Cyclopentane	0.22	cis,trans-, cis-1,2,3-Trimethylcyclopentane	0.46
Methylcyclopentane	0.82	cis-trans-cis-1,2,4-Trimethylcyclopentane	0.57
cis-1,3-Dimethylcyclopentane	0.79	cis,cis,cis-1,2,3-Trimethylcyclopentane	0.18
trans-1,2-Dimethylcyclopentane	1.03	Propylcyclopentane	0.86
trans-1,3-Dimethylcyclopentane	0.14	Isopropylcyclopentane	0.25
cis-1,2-Dimethylcyclopentane	0.22	1-Methyl-3-propylcyclopentane	0.25
Ethylcyclopentane	0.13		
		Total	5.93

TABLE 1 (continued)

Name of hydrocarbon	Content (% by wt. on gasoline)	Name of hydrocarbon	Content (% by wt. on gasoline)
Cyclohexanes			
Cyclohexane	0.61	1,1-Dimethylcyclohexane	0.16
Methylcyclohexane	2.79	1,1,2-Trimethylcyclohexane	Traces
1,3-Dimethylcyclohexane	0.87	1,1,3-Trimethylcyclohexane	2.68
1,4-Dimethylcyclohexane	0.34	1,1,4-Trimethylcyclohexane	Traces
1,2-Dimethylcyclohexane	0.30		
Ethylcyclohexane	1.18		
		Total	8.93
Aromatics			
Benzene	0.28	p-Xylene	0.28
Toluene	0.88	o-Xylene	0.18
m-Xylene	0.83	Ethylbenzene	0.55
		Total	3.00
		Identified	84.36
		Not identified	6.07
		Losses	9.57

We investigated the gasoline boiling up to 150°, which was obtained from a wide distillate (from start of boil to 240°). From the wide distillate we separated the low-boiling part (from start of boil to 60°) and the 60-205° fraction. From the latter we distilled narrow fractions up to 200° for investigation. The investigation of the ligroin fraction (150-200°) is described in the preceding communication [2]. The hydrocarbons detected in the gasoline by the combined method [3] and their amounts are indicated in Table 1.

The group composition of the gasoline is given in Table 2.

It follows from Table 2 that the gasoline from Shugurov petroleum contains 66.5% of paraffin and 15% of naphthene hydrocarbons. This gasoline can therefore be described as a paraffinous gasoline. The high contents of pentane (10%) and octane are noteworthy. As a rule, almost in all gasolines (with the exception of the gasoline from Devonian petroleum DIII, bore hole 641) the octane content is less than the heptane content. There is a predominance of normal paraffins (35%) over isoparaffins (30%), whereas in the carboniferous petroleum (bore hole 426) the reverse is true (29% and 35%, respectively). This is due to the fact that, in comparison with other petroleums of the Shugurov deposit, the petroleums from bore holes 10, 104, and 6 contain considerable amounts of light fractions; in particular, petroleum from bore hole 10 contains 2.4% of fractions boiling up to 60° [4]. The high contents of pentane and octane do not imply that the Shugurov gasoline from bore hole 10 is peculiar in this respect, inasmuch as it does not otherwise differ in chemical composition from other gasolines, both from the carboniferous and from the Devonian deposits. In this respect it will be of interest to compare the individual hydrocarbon composition of the carboniferous gasoline from bore hole 5 of the Shugurov deposits in which the collectors are carbonate rocks.

TABLE 2.

Class of hydrocarbons	Content (% by wt. on gasoline)
Normal paraffins	34.8
Paraffins with tertiary carbon atom	30.4
Paraffins with quaternary carbon atom	1.3
Cyclopentanes	5.9
Cyclohexanes	8.9
Aromatics	3.0

SUMMARY

1. An investigation was made of the individual hydrocarbon composition of the gasoline of Shugurov petroleum (bore hole 10), which is associated with the carboniferous system with carbonate rocks as collector.

2. The high content of pentane is noteworthy; it is to be explained by the considerable content of light fractions (up to 60°) in the petroleum from bore hole 10.

FREE-RADICAL ADDITION OF CYCLOPENTANONE AND CYCLOHEXANONE TO α-OLEFINS AND ALLYL ETHERS

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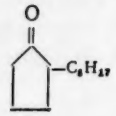
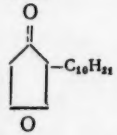
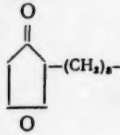
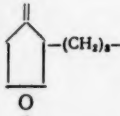
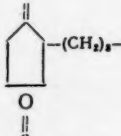
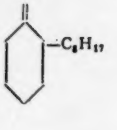
Several variants of the synthesis of aliphatic carboxylic acids by the cleavage of five- and six-membered alicyclic compounds have been used. Fieser [1] proposed to oxidize 1-alkylcyclopentanols and 1-alkylcyclohexanols with chromium trioxide in glacial acetic acid, as a result of which 5- and 6-keto carboxylic acids, respectively, are formed. The 1-alkylcycloalkanols required were synthesized by the reaction of Grignard reagents with cyclic ketones. However, in almost all cases yields of only 10-15% were obtained in the oxidation of 1-alkylcyclopentanols and 1-alkylcyclohexanols to keto acids [2-4]. Much better results were obtained by the ozone oxidation of products of the dehydration of tertiary alcohols, namely 1-alkylcyclohexenes and 1-alkylcyclopentenes [5,6].

TABLE 1.

Expt.	Reactants		Amount taken (mol. proportion)			Temp., °C	Time, (hr)	Yield			Residue, g
	Ketone (A)	Unsaturated compound (B)	A	B	peroxide			g	% on B taken	% on B that reacted	
1	Cyclopentane	1-Octene	3	0.3	0.06	128-130	6.5	33	57	61	13.5
2	"	1-Decane	3	0.3	0.06	127-130	6.5	47.8	71	–	13.5
3	"	4-Methyl-1-decene	3.5	0.35	0.07	128-130	6	51.7	62	68	14
4	"	Allyl octyl ether	3.5	0.35	0.105	128-129	6	47.2	53	59	20
5	"	Allyl decyl ether	3	0.3	0.06	129-130	6	38.1	45	59	19.5
6	Cyclohexanone	1-Octene	3	0.3	0.06	142-150	4.5	37.2	59	76	11.5
7	"	1-Decene	3	0.3	0.06	146-152	6	44.5	62.3	–	14.5
8	"	4-Methyl-1-decene	3.5	0.35	0.07	149-153	6	54	61.2	–	16
9	"	Allyl octyl ether	3.5	0.35	0.105	143-152	6	53.5	57	64	23
10	"	2-(Allyloxy)-ethanol	5	0.5	0.1	142-153	6	30	30	–	37.5

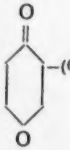
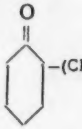
Another known method for the synthesis of 6- and 7-keto carboxylic acids consists in the acylation of cyclopentanone and cyclohexanone with acid anhydrides [7] and cleavage of the resulting 2-acylcyclopentanones and 2-acylcyclohexanones with alkali [8]. An unsatisfactory feature of this last method is the low yield (about 35%) of product at the acylation stage. The synthesis of 2-acylcyclohexanones in 75-85% yield has been developed by Hunig and co-workers [9], who carried out the acylation of not cyclohexanone itself, but the product of its condensation with morpholine or pyrrolidine. In this case the scheme of synthesis is complicated on account of additional stages, namely the formation of the enamine and its hydrolysis. A method of lengthening the chain of a carboxylic acid by five carbon atoms was proposed by Plesek [10]. It consisted in the acylation of ethyl 2-oxocyclopentanecarboxylate with an acid chloride and the subsequent cleavage of the acylated product to a 6-keto acid. Finally, we must

TABLE 2.

Expt.	1:1 Adduct	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p. of semicarbazone (°C)	M.p. of 2,4-dinitrophenylhydrazone (°C)
1 *		96—97 (1,5)	0,8820	1,4530	60,16	60,21	79,30 79,27	12,01 12,11	79,53	12,32	184,6—185	105,8—106,2
2 *		106—108 (1)	0,8768	1,4558	69,54	69,51	80,23 80,41	12,42 12,52	80,29	12,58	182,5—183	—
3		128—130 (1)	0,8775	1,4580	74,13	74,15	80,53 80,62	12,60 12,80	80,61	12,68	165	—
4		136—137 (1)	0,9098	1,4560	76,01	75,94	75,52 75,34	11,85 11,61	75,54	11,89	—	—
5		154—155 (1)	0,9039	1,4574	85,17	85,23	76,67 76,83	12,07 12,10	76,54	12,13	—	—
6 *		100—101(1,5)	0,8942	1,4605	64,49	64,88	—	—		—	109—109,5	118—118,5

(continued)

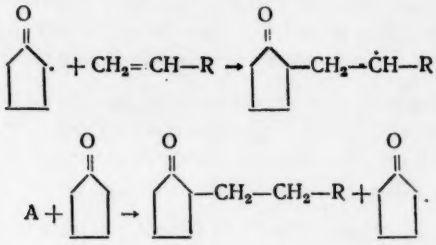
TABLE 2 (continued)

Expt.	1:1 Adduct	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calc.	Found, % C	Found, % H	Calculated, % C	Calculated, % H	M.p. of semicarbazone (°C)	M.p. of 2,4-dinitrophenylhydrazone (°C)
7		119—120 (1)	0,8819	1,4606	74,13	74,18	80,32 80,37	12,53 12,52	80,60	12,68	104,5—105	
8		122—123 (1)	0,8826	1,4625	78,70	78,83	81,04 81,28	13,11 12,93	80,88	12,78	85	—
9		175—177(2,5)	0,9129	1,4600	80,58	80,61	75,88 75,74	11,85 11,89	76,06	12,01	—	—
10		130—132 (1)	1,0464	1,4789	54,27	54,25	65,67	9,98	65,96	10,06	—	—

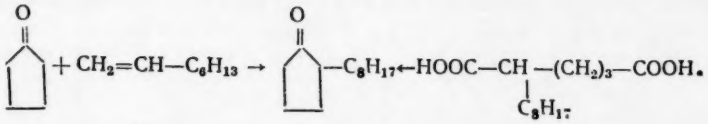
• Data from literature: 1) b.p. 156° (20 mm); d^{20}_4 0.8850; $n^{20}D$ 1.4535; semicarbazone, m.p. 185.5-186° [14]; 2) b.p. 182° (20 mm); d^{20}_4 0.8791; $n^{20}D$ 1.4559; semicarbazone, m.p. 183° [14]; 6) b.p. 75-78° (0.05 mm); d^{20}_4 0.88; $n^{20}D$ 1.4580; 2,4-dinitrophenylhydrazone, m.p. 112-113° [12]. The other substances were prepared for the first time.

mention the synthesis developed by Stetter [11] and applied in numerous cases for the synthesis of carboxylic acids by the alkylation of 1,3-cyclohexadione and the cleavage of the resulting 2-alkyl-1,3-cyclohexadiones with hydrazine.

We set ourselves the task of developing another route to keto carboxylic acids which, as we saw it, would be preferable to those described above in quite a number of cases. With this object we studied the free-radical addition of cyclopentanone and cyclohexanone to α-olefins and allyl ethers. The addition of cyclohexanone to 1-octene initiated by ultraviolet radiation was described earlier by Kharasch and co-workers [12]; they showed that, when a 1:8 mixture of cyclohexanone and 1-octene was irradiated for 50-70 hr, a number of products was formed: hexanal, 2-octene, octene dimer, 2-octylcyclohexanone, 2:1 and 3:1 adducts, and macromolecular substances. The yield of 2-octylcyclohexanone was 20-26% on the cyclohexanone. Using t-butyl peroxide as initiator, we showed that cyclohexanone and cyclopentanone add to undecenoic acid with formation of 11-(2-oxocyclopentyl)undecanoic and 11-(2-oxocyclohexyl)undecanoic acids, respectively [13]. In the present work this reaction was studied in greater detail. The conditions of individual experiments, the yields of 1:1 adducts, and the amounts of high-boiling products are given in Table 1. Table 2 shows the structures of the 2-substituted cyclopentanones and cyclohexanones obtained, and their properties. Experiments 1-10 were all carried out in the same way: a solution of the peroxide and unsaturated compound were added uniformly and continuously throughout the whole reaction to the boiling ketone. Reaction began with homolytic decomposition of t-butyl peroxide into t-butoxy radicals. On reaction with the ketone these abstracted hydrogen from the CH_2 group adjacent to the carbonyl group. Such selectivity in the direction of the attack on the ketone molecule is probably to be explained by the lower dissociation energy of the α-C – H bonds and the greater stability of the resulting radical resulting from the conjugation effect. The radical formed adds at the double bond of the unsaturated compound, after which propagation of the chain proceeds:

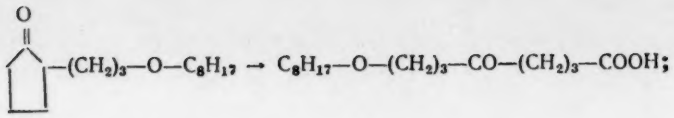


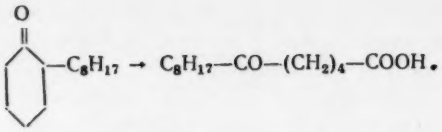
As well as the 1:1 adduct, substances of higher molecular weight are obtained, and these are probably products of the addition of the 1:1 adduct to a new olefin molecule and telomerization products. At molar proportions of ketone: unsaturated compound:peroxide of 10:1:0.2, the yields of 1:1 adducts were 50-70%, calculated on the unsaturated compound. In Experiments 1, 3-6, and 9 part of the olefins and allyl ethers taken for reaction were isolated from the reaction mixture, but in the other experiments we did not succeed in doing this. In carrying out the identification of the products we found that the 2,4-dinitrophenylhydrazones of 2-octylcyclohexanone prepared by Kharasch [12] and by us had different melting points (112-113° and 118-118.5°, respectively). To confirm the correctness of the structure that we attributed to the 1:1 adducts (see Table 2), we synthesized 2-octylcyclopentanone in two ways:



The two samples had identical properties and their melting points were identical and were not depressed in a mixture test.

It is evident that under the conditions of irradiating the mixture of 1-octene and cyclohexanone with ultraviolet radiation, cyclohexanone adds not only to 1-octene, but also to the 2-octene formed. As a result, a 1:1 adduct is obtained which consists mainly of 2-octylcyclohexanone contaminated by isomeric products. It is this that explains the low melting point of the 2,4-dinitrophenylhydrazone. Under our conditions the probability of the formation of 2-octene was very low. The 1:1 adducts obtained in Experiments 1-8 were oxidized with chromium trioxide with cleavage of the ring and formation of the corresponding keto acids, e.g.





All the oxidations were carried out under identical conditions; the chromium trioxide was taken in an amount that exceeded the theoretical by about 15%. The highest yield of keto carboxylic acids was obtained in the oxidation of 2-alkylcyclopentanones and 2-alkylcyclohexanones (77-87%). Lower yields of keto acids were obtained when branching or an ether link was present in the side chain.

EXPERIMENTAL

Addition of Cyclopentanone and Cyclohexanone to α-Olefins and Allyl Ethers (Table 1, Experiments 1-10). Cyclopentanone or cyclohexanone, in an amount of 80-85 moles percent of the total calculated quantity, was placed in a flask fitted with stirrer, reflux condenser, calibrated dropping funnel, and thermometer. The ketone was heated to the boiling point and stirred while uniform dropwise addition was made of a solution of the t-butyl peroxide and the olefin (or allyl ether) in the remainder of the ketone. When the addition was complete, the reaction mixture was heated further for 1 hr; excess of ketone and products of the decomposition of the peroxide were then distilled off. From the resulting high-boiling product we vacuum-distilled the 1:1 adduct, and telomerization products remained in the flask; the amounts are given in Table 1 in the column "Residue." The 1:1 adducts were purified by repeated distillation. In Experiments 3-5 and 7-9, they were also passed through a column of silica gel. In Experiments 1, 3-6, and 9 we succeeded in isolating the unsaturated compounds that did not react.

2-Octylcyclopentanone. A well-ground mixture was prepared from 14 g (0.05 mole) of 2-octyladipic acid (the synthesis of this was described earlier [15]) and 1.7 g of barium hydroxide. The mixture was heated in the range 270-300°, and ketone and water distilled off. We obtained 6 g (56%) of 2-octylcyclopentanone; b.p. 122-129° (4 mm); d^{20}_4 0.8816; $n^{20}D$ 1.4529. Its 2,4-dinitrophenylhydrazone had m.p. 105.7-106.2° (from alcohol).

5-Oxotridecanoic Acid (11). To a solution of 26 g of concentrated sulfuric acid in 44 ml of water we added 19.6 g (0.1 mole) of 2-octylcyclopentanone and then, with stirring, a solution of 15 g (0.15 mole) of chromium trioxide and 26 g of sulfuric acid in 44 ml of water. During the addition the temperature was kept in the range 45-50°, and the mixture was then kept at the same temperature for 2 hr further and left overnight. By extraction with hot benzene (six portions, each 50-60 ml) and then with ether, the keto acid was isolated from the reaction mixture. Ether and part of the benzene were driven off, and the precipitated crystals of keto acid (16.8 g) were separated from the mother liquid. Distillation of the mother liquid gave a further 1.5 g of the acid. In all we obtained 18.3 g (80%) of 5-oxotridecanoic acid, m.p. 72-72.5° (from benzene). Found: C 68.39, 68.15; H 10.67, 10.64%. $C_{13}H_{24}O_3$. Calculated: C 68.38; H 10.60%. The other keto acids were prepared from 2-substituted cyclopentanones and cyclohexanones by an analogous procedure.

5-Oxopentadecanoic Acid (12). On oxidation of 40 g (0.18 mole) of 2-decylcyclopentanone with 27 g (0.27 mole) of chromium trioxide we obtained 35.5 g (77%) of 5-oxopentadecanoic acid, m.p. 82-82.5° (from benzene). Found: C 70.21; 70.23; H 11.31, 11.06%. $C_{15}O_{28}O_3$. Calculated: C 70.27; H 11.01%. Semicarbazone m.p. 121 to 121.5° (from alcohol).

9-Methyl-5-oxopentadecanoic Acid (13). From 47.9 g (0.2 mole) of 2-(4-methyldecyl)cyclopentanone we obtained 48 g of crude keto acid. After vacuum distillation and purification through a silica gel column we isolated 36 g (66% on reactant taken, 79% on the amount that reacted) of 9-methyl-5-oxopentadecanoic acid; b.p. 175-17 ° (1 mm), d^{20}_4 0.9497, $n^{20}D$ 1.4578; found MR 77.66; calculated MR 77.88; acid number found 205.5, calculated 207.5. Found: C 70.76; H 11.18%. $C_{16}H_{30}O_3$. Calculated: C 71.07; H 11.18%. Semicarbazone m.p. 113.5-114° (from alcohol).

8-(Octyloxy)-5-oxooctanoic Acid (14). On oxidation of 38.2 g (0.15 mole) of 2-[3-(octyloxy)propyl]cyclopentanone we isolated 15.5 g of unchanged reactant and 14.3 g of 8-(octyloxy)-5-oxooctanoic acid. Yield 33.3% on reactant taken and 56% on the amount that reacted; m.p. 49° (from acetone). Found: C 67.20, 67.23; H 10.56, 10.66%. $C_{16}H_{30}O_4$. Calculated: C 67.10; H 10.56%. Semicarbazone m.p. 90-90.5° (from alcohol).

8-(Decyloxy)-5-oxooctanoic Acid (15). On oxidation of 28.3 g (0.1 mole) of 2-[3-(decyloxy)propyl]cyclopentanone we isolated 13 g of unchanged reactant and 9.8 g (31% on reactant taken, 58% on the amount that reacted) of 8-decyloxy-5-oxooctanoic acid, m.p. 58.1° (from acetone). Found: C 68.66, 68.67; H 10.70, 10.80%. $C_{18}H_{34}O_4$. Calculated: C 68.75; H 10.90%. Semicarbazone m.p. 108° (from alcohol).

6-Oxotetradecanoic Acid (16). From 17.8 g (0.085 mole) of 2-octylcyclohexanone we obtained 18 g (87%) of 6-oxotetradecanoic acid, m.p. 72.5° (from acetone). Semicarbazone m.p. 129-130° (from alcohol).

For the melting point of the keto acid the literature gives 71.5° [4] and 72° [10]; for the melting point of the semicarbazone it gives 130° [4] and 138° [10].

6-Oxohexadecanoic Acid (17). From 38.2 g (0.16 mole) of 2-decylcyclohexanone we obtained 30 g (69.3% on the reactant taken and 84.7% on the amount that reacted) of 6-oxohexadecanoic acid, m.p. 81.5-82° (from benzene). Found: C 71.29, 71.17; H 11.12, 11.16%. $C_{16}H_{30}O_3$. Calculated: C 71.07; H 11.18%. Semicarbazone m.p. 154° (from alcohol). The literature [4] gives: keto acid m.p. 79°, semicarbazone m.p. 149.5°.

10-Methyl-6-oxohexadecanoic Acid (18). From 46.7 g (0.185 mole) of 2-(4-methyldecyl)cyclohexanone we obtained 45.8 g of crude keto acid. After distillation and purification through a silica gel column we obtained 26 g (50% on the reactant taken and 63% on the amount that reacted) of 10-methyl-6-oxohexadecanoic acid; b.p. 181 to 182° (1 mm); d^{20}_4 0.9439; $n^{20}D$ 1.4587; found MR 82.33; calculated MR 82.53. Found: C 71.61, 71.43; H 11.48, 11.27%. $C_{17}H_{32}O_3$. Calculated: C 71.78; H 11.34%. Semicarbazone m.p. 103° (from alcohol).

Acids (11), (13)-(15), and (18) were prepared for the first time.

SUMMARY

A new method was developed for the synthesis of 5- and 6-keto carboxylic acids by the addition of cyclopentanone and of cyclohexanone in presence of t-butyl peroxide to α-olefins with subsequent oxidation of the 2-alkylcyclopentanones and 2-alkylcyclohexanones with chromium trioxide.

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VINYL COMPOUNDS IN THE DIENE SYNTHESIS

COMMUNICATION 8. DIENE CONDENSATION OF VINYL ETHERS AND SULFIDES WITH ANTHRACENE

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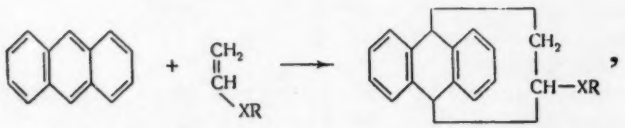
In a systematic study of the dienophilic properties of vinyl ethers we reported [1-4] their ability to undergo diene condensation with some cyclic and acyclic dienes. We noted that the diene synthesis goes more readily with vinyl ethers containing cyclic groups, and of the dienes investigated it is the cyclic compounds that undergo the reaction most readily. In the case of an acyclic diene such as 2,3-dimethyl-1,3-butadiene considerably lower yields of adducts were obtained than in the case of hexachlorocyclopentadiene. This fact is to be explained partly by the higher tendency of acyclic dienes to polymerize. In the case of 2,3-dimethyl-1,3-butadiene we obtained a considerable amount of the copolymer of vinyl ether and 2,3-dimethyl-1,3-butadiene.

With a view to the more complete investigation of the dienophilic activity of vinyl ethers and sulfides it was of interest to study the diene condensation of these with polycyclic hydrocarbons having conjugated systems of double bonds. As our conjugated aromatic system we chose anthracene as being the most readily available and highly reactive. The central ring of the anthracene nucleus contains an active diene system and reacts smoothly with maleic anhydride [5-7], dimethyl acetylenedicarboxylate [5], allyl alcohol [8], and other dienophiles [9] with formation of stable adducts.

Diene condensation with anthracene was carried out with butyl vinyl, hexyl vinyl, cyclohexyl vinyl, phenyl vinyl, m-tolyl vinyl, decyl vinyl, decahydro-2-naphthyl vinyl, and 2-naphthyl vinyl ethers, and also with ethyl vinyl and phenyl vinyl sulfides. Reaction went according to the scheme:



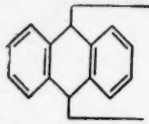
XR=OC_4H_9 (I); OC_6H_{13} (II); OC_6H_{11} (III); OC_6H_5 (IV), $OC_6H_4CH_3$ (*m*) (V); $OC_{10}H_{21}$ (VI); $OC_{10}H_{17}$ (β) (VII); $OC_{10}H_7$ (β) (VIII); SC_2H_5 (IX); SC_6H_5 (X).

The diene synthesis was carried out in a steel ampoule, which was heated at 220-240° for 13-15 hr. With vinyl sulfides the reaction was carried out at 180°. Phenyl vinyl ether showed the greatest dienophilic activity. Rise in the reaction temperature led to resinification of the products and lowering of the yield of the adduct, and lowering of the temperature slowed down the reaction.

EXPERIMENTAL

Reaction of Hexyl Vinyl Ether with Anthracene. A mixture of 17.28 g (0.135 mole) of hexyl vinyl ether and 4 g (0.0225 mole) of anthracene, m.p. 216°, was placed in a steel ampoule; the latter was purged with nitrogen, after which the mixture was heated at 235° for 14 hr. The product was discharged and filtered through a glass filter to separate a crystalline solid (1.1 g), which, after three crystallizations from heptane at 45-50°, was found to be unchanged anthracene, m.p. 216°. Excess of hexyl vinyl ether and the acetal that had formed were distilled from the filtrate. The residue (4.4 g) was vacuum-fractionated, and the following fractions were collected: Fraction I, b.p.

Characterization of Adducts Formed by Vinyl Ethers and Sulfides with Anthracene

Compound	XR in the formula 	B.p. in °C (p in mm)	M.p. (°C)	F.p. (°C)	n_D^{20}	Found, %			Molecular formula	Calculated, %			Yield (% on anthracene that reacted)
						C	H	S		C	H	S	
I	OC_4H_9	157 (1,5)	47,5—49 (from alcohol)	—	1,5770	86,26 86,30	8,12 8,09	— —	$C_{20}H_{22}O$	86,33	7,91	—	75,7
II	OC_6H_{13}	157 (1)	—	—30	1,5569	86,14 86,23	8,74 8,82	—	$C_{22}H_{26}O$	86,27	8,49		77,6
III	OC_6H_{11}	135—137 (0,001)	86,5—87,5 (from alcohol)	—	—	86,61 86,72	8,13 8,16	—	$C_{22}H_{24}O$	86,84	7,89	—	79,7
IV	OC_6H_5	—	122,5—124 (from heptane)	—	—	88,58 88,63	5,75 5,74	—	$C_{22}H_{18}O$	88,59	6,04	—	90,2
V	$OC_6H_4CH_3(m)$	—	138—139,5 (from pet. ether)	—	—	88,20 88,18	6,57 6,52	—	$C_{23}H_{20}O$	88,46	6,41	—	85,7
VI	$OC_{10}H_{21}$	197 (1)	—	—37	1,5410	86,27 86,07	9,60 9,55		$C_{26}H_{34}O$	86,18	9,39	—	68,1
VII	$OC_{10}H_{17}$ (β)	170 (0,009)	—	+7	1,547[illegible]	86,83 86,79	8,29 8,32		$C_{26}H_{30}O$	87,15	8,38	—	67,8
VIII	$OC_{10}H_7$ (β)	—	119—120 (from pet. ether + diethyl ether)		—	89,79 89,57	5,74 5,76	—	$C_{26}H_{20}O$	89,65	5,74	—	66,4
IX	SC_2H_5	172 (2)	—	—10	1,6210 1,5557	80,82 80,79 63,95	6,90 7,04 5,66	12,28 12,29 10,39	$C_{13}H_{18}S$	81,2	6,76	12,0[illegible]	65
X	SC_6H_5	194 (2)	—			83,87	5,64	10,45	$C_{22}H_{18}S$	84,07	5,73	10,19	64,6

up to 155° (1 mm), 0.8 g; Fraction II, b.p. 156-157° (1 mm), 3.2 g; residue, 0.4 g. From Fraction I we isolated anthracene (0.5 g), m.p. 216°. After redistillation Fraction II was found to be the adduct (II) formed by hexyl vinyl ether with anthracene (see table).

In an analogous way we prepared the other adducts formed by vinyl ethers with anthracene. The adducts of phenyl vinyl (IV), m-tolyl vinyl (V), and 2-naphthyl vinyl (VIII) ethers were purified by fractional crystallization from heptane, petroleum ether, and a mixture of 80% of petroleum ether and 20% of diethyl ether, respectively. The adduct of butyl vinyl ether (I) may remain liquid for a long time at room temperature and crystallize out only when cooled strongly (−30°). All the crystalline adducts were soluble in benzene, acetone, and ether and difficultly soluble in alcohol, heptane, and petroleum ether. The liquid adducts were thick and viscous with the violet fluorescence characteristic for compounds of the anthracene series.

SUMMARY

1. The conditions were studied for the diene condensation of anthracene with butyl vinyl, hexyl vinyl, cyclohexyl vinyl, phenyl vinyl, m-tolyl vinyl, decyl vinyl, decahydro-2-naphthyl vinyl, and 2-naphthyl vinyl ethers, and also with ethyl vinyl and phenyl vinyl sulfides.

2. Ten adducts, which were new 9,10-dihydroanthracene derivatives, were isolated and characterized.

3. Vinyl ethers and sulfides show greater dienophilic activity toward anthracene than toward acyclic dienes and less activity than toward cyclopentadiene and hexachlorocyclopentadiene.

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SYNTHESIS AND POLYMERIZATION OF DIALLYL TARTRATE

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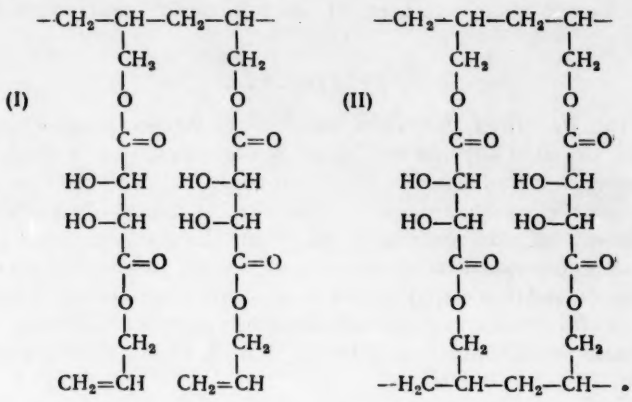
There are descriptions in the literature [1-4] of the polymerization of some diallyl esters of dibasic acids (succinic, adipic, maleic, fumaric, and phthalic). Data on diallyl tartrate are confined to the patent literature [5], which indicates the possibility of its polymerization in presence of benzoyl peroxide. We considered it to be of interest to investigate this reaction and determine the effect of the structure of diallyl tartrate, which contains functional groups other than allyl (OH), on the course of the polymerization and on the properties of the polymer. To establish the procedure in the polymerization of diallyl tartrate, the reaction was carried out in presence of various amounts of initiators (benzoyl peroxide and azodiisobutyronitrile), the temperature and reaction time being varied. As a result of the investigations it was shown that, depending on the reaction conditions, linear (I) and three-dimensional (II) diallyl tartrate polymers are formed in various proportions:



The effect of the amount of initiator (benzoyl peroxide) on the course of the polymerization is shown in Table 1. This shows that with 2% of benzoyl peroxide polymerization is very slow: the amount of polymer isolated

TABLE 1. Polymerization of Diallyl Tartrate in Presence of Various Amounts of Benzoyl Peroxide at 95° for 5 hr

Content of $(PhCO)_2O_2$, (%)	Amount of polymer taken for fractionation (g)	Yield of polymer (%)			Amount of unchanged monomer (%)	Tartaric acid content of cross-linked polymer (%)	
		total	cross-linked	linear		found	calc.
2	1,32	5,3	—	5,3	94,7	—	—
3	1,75	29,18	17,75	11,43	61,2	49,7	50,5
4	2,65	59,71	58,2	1,51	38,5	49,3	50,5
5	2,57	57,26	56,1	1,16	39,7	49,8	50,5
6	2,47	56,71	55,1	1,21	40,5	48,7	50,5

is only 5% on the monomer taken. This polymer is soluble in methanol. When the amount of benzoyl peroxide is increased, there is an increase in the yield and in the content of cross-linked polymer. Thus, in presence of 3% of benzoyl peroxide the yield attains 29%, and of this 11.4% is soluble polymer and 17.75% is cross-linked polymer; in presence of 4%, 5%, and 6% of benzoyl peroxide the greatest yields of polymers (57-60%) are obtained, and these are mainly of cross-linked structure (yield 55-58%). In all cases the composition of the polymers is close to theoretical (see Table 1). Polymerization was carried out also at various temperatures (60°, 95°, and 125°) with reaction times of 5-21 hours (Table 2). As would be expected, rise in temperature and increase in the time of heating affects the process greatly. Thus, with the same amount of initiator (6%) and a reaction time of 5 hr, diallyl tartrate scarcely polymerizes at all at 60°, whereas at 95° it forms a solid insoluble polymer in 57% yield. The preparation of such a polymer at 60° requires 21 hr heating. Better results were obtained when the polymerization was carried out with 6% of benzoyl peroxide at 125° for 18 hr. The yield of clear solid cross-linked polymer was 98%; it had the property of not becoming charged with static electricity on being rubbed. The thermostability value of the polymer was 294°. The use of azodiisobutyronitrile as initiator gave worse results than benzoyl peroxide. In presence of 6% of azodiisobutyronitrile at 95° for 18 hr, diallyl tartrate reacted with only 5% conversion into a viscous polymer. Diallyl tartrate is less active in polymerization than the fumeric and maleic esters [1], which is probably associated with the presence of hydroxy groups in diallyl tartrate.

TABLE 2. Polymerization of Diallyl Tartrate at Various Temperatures for Various Reaction Times*

Amt. of initiator (%)	Reaction time (hr)	Reaction temp., (°C)	Yield of polymer (%)
6 (BP)	5	60	–
6 (BP)	5	95	57.0
6 (BP)	21	60	57.0
6 (BP)	18	125	98.0
36 (ADIBN)	18	95	5.0

*BP = benzoyl peroxide; ADIBN = azodiisobutyronitrile.

EXPERIMENTAL

Synthesis of Diallyl Tartrate. The synthesis was carried out by the esterification method, as follows. A mixture of 50 g of tartaric acid, 135 ml of allyl alcohol, 200 ml of benzene, 0.3 g of hydroquinone, and 1 ml of sulfuric acid as catalyst (this was added as the mixture was stirred) was introduced into a three-necked flask fitted with stirrer and reflux condenser. The reaction was carried out at 70° for 5 hr. At the end of the reaction allyl alcohol, benzene, and water were vacuum-distilled off. The resulting diallyl tartrate was dissolved in ether, and the solution was washed with 10% sodium carbonate solution and then water until neutral. It was dried over anhydrous sodium sulfate for 24 hr; ether was distilled off, and then diallyl tartrate under a vacuum; yield 43.8 g (56%). Diallyl tartrate is a clear colorless viscous liquid with a feeble characteristic odor. It is unchanged after long standing; b.p. 162° (4 mm); $n^{20}D$ 1.4738; d^{20}_4 1.1979; Found MR 53.99; calculated MR for $C_{10}H_{14}O_6$ 53.80. The literature [6] gives b.p. 171° (10 mm), d^{20} 1.1941.

Polymerization of Diallyl Tartrate. In the study of the polymerization of diallyl tartrate (DAT) the freshly synthesized product was used. As initiators for the reaction we used benzoyl peroxide (2-6%) and azodiisobutyronitrile (6%). The polymerization was carried out in glass ampoules with heating to 60°, 95°, and 125° for 5, 18, and 21 hr. In the polymerization there was a change in the color of the reaction products. The colorless monomer first became brown, and toward the end of the reaction the polymer became light yellow. In the course of the polymerization the viscosity gradually rose, after which there formed a gel, which was converted into solid polymer. At the end of the reaction the ampoules were opened and their contents were treated with methanol; part of the polymer then dissolved, and the remainder only swelled. The mixture of polymers was then treated with ether to separate polymer from monomer. Reprecipitation was repeated until there was no longer a reaction for a double bond. The polymers isolated were treated with methanol to separate soluble from insoluble polymer. After separation the polymers were dried to constant weight. The methanol-soluble polymer contained a free allyl group, which was confirmed by the reaction with bromine water and by the infrared spectrum. We obtained bands of moderate intensity at 1652 cm^{-1}, which were due to the valence vibrations of a terminal double carbon bond. The methanol-insoluble polymer was probably of cross-linked structure, for it was insoluble in organic solvents and decomposed without melting. The structure of the polymers was established by hydrolysis with alkali and subsequent titration. By distillation of the solutions obtained after reprecipitation of the polymers we isolated unchanged monomer. The results of the experiments are given in Tables 1 and 2.

SUMMARY

1. Diallyl tartrate was synthesized, and its polymerization was studied.

2. The effects of the amount of benzoyl peroxide, the temperature, and the reaction time on the yields of linear and cross-linked polymer were determined.

3. The cross-linked diallyl tartrate polymer has the property of not becoming charged with static electricity when rubbed.

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BRIEF COMMUNICATIONS

COMPLEXES OF DECABORANE WITH ORGANIC PHOSPHORUS AND ARSENIC COMPOUNDS

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According to the literature, decaborane is able to form complexes with various electron-donating compounds, for example, with tertiary amines, triphenylphosphine, acetonitrile, diethylcyanamide, etc. [1-3]. The reaction occurs according to the following equations:

$$B_{10}H_{14}+2CH_3CN \longrightarrow B_{10}H_{12}[CH_3CN]_2+H_2$$
$$B_{10}H_{14}+2P(C_6H_5)_3 \longrightarrow B_{10}H_{12}[(C_6H_5)_3P]_2+H_2$$
$$B_{10}H_{14}+2(C_2H_5)_2NCN \longrightarrow B_{10}H_{12}[(C_2H_5)_2NCN]_2+H_2.$$

2-Isopropyl- and 2-methyl-5-(2-chloroethyl)tetrazoles react with decaborane similarly [4]:

$$B_{10}H_{14}+2C_4N_4H_8 \longrightarrow B_{10}H_{12}(C_4N_4H_8)_2+H_2.$$

In the present work, we studied the reaction of decaborane with trialkyl- and triaryl-derivatives of group five elements: P, As, and Sb. The reaction of triethylphosphine with decaborane occurred energetically with evolution of heat, vigorous hydrogen evolution, and complex formation according to the scheme:

$$B_{10}H_{14}+2(C_2H_5)_3P \longrightarrow C_{10}H_{12}[(C_2H_5)_3P]_2+H_2.$$

The reaction with triethylarsine occurred similarly, but the reaction took place only on heating (60-80°):

$$B_{10}H_{14}+2(C_2H_5)_3As \longrightarrow B_{10}H_{12}[(C_2H_5)_3As]_2+H_2.$$

On heating triethylstibene with decaborane at 150°, the corresponding complex could not be isolated although gas evolution was observed. It was shown that by heating diphenylchlorophosphine with decaborane in benzene, a complex was formed as in the case of triphenylphosphine:

$$2(C_6H_5)_2PCl + B_{10}H_{14} \rightarrow B_{10}H_{12}[(C_6H_5)_2PCl]_2 + H_2.$$

Phenyldichlorophosphine does not form a complex with decaborane either in boiling benzene or in toluene. Triphenylarsine forms a complex with decaborane with evolution of the theoretical amount of hydrogen only at 110° (in toluene). However, the complex partially decomposes upon prolonged heating:

$$B_{10}H_{14} + (C_6H_5)_3As \rightarrow B_{10}H_{12}[(C_6H_5)_3As]_2 + H_2.$$

Triphenylstibene and triphenylbismuthine do not react with decaborane upon boiling in toluene. It was established that triethylphosphine, diphenylchlorophosphine, and triethylarsine take part in an exchange reaction with diacetonitriledecaborane, as a result of which the corresponding complexes are isolated in the latter two cases:

$$B_{10}H_{12}(CH_3CN)_2 + 2As(C_2H_5)_3 \rightarrow B_{10}H_{12}[(C_2H_5)_3As]_2 + 2CH_3CN,$$
$$B_{10}H_{12}(CH_3CN)_2 + 2(C_6H_5)_2PCl \rightarrow B_{10}H_{12}[(C_6H_5)_2PCl]_2 + 2CH_3CN.$$

EXPERIMENTAL

Reaction of Triethylphosphine with Decaborane. To a solution of 0.6 g (0.005 M) of decaborane in 20 ml of ether or benzene in a nitrogen atmosphere was added an ethereal or benzene solution of 1.4 g (0.015 M) of triethylphosphine. An exothermic reaction and vigorous hydrogen evolution took place upon mixing. The reaction mixture was heated on a water bath until hydrogen evolution stopped (120 ml of hydrogen was collected). The solvent was distilled under vacuum and the residue was washed with ether to remove excess triethylphosphine. Bis-(triethylphosphine)-decaborane melted at 110° after three recrystallizations from methylene chloride. Found: C 40.29, 40.44; H 11.84, 11.92%. $C_{12}H_{42}B_{10}P_2$. Calculated: C 40.45; H 11.79%.

Reaction of Triethylarsine with Decaborane. Corresponding to the previous experiment, bis-(triethylarsine)-decaborane was obtained from 0.6 g (0.005 M) of decaborane and 2.0 g (0.012 M) of triethylarsine by heating in benzene. The theoretical amount of hydrogen (120 ml) was evolved. After three recrystallizations from a methylene chloride – ether mixture, bis-(triethylarsine)decaborane melted at 140-141°. Found: C 32.42, 32.39; H 9.37, 9.48%. $C_{12}H_{42}B_{10}As_2$. Calculated: C 32.15; H 9.37%.

Reaction of Diphenylchlorophosphine with Decaborane. As described above, bis-(diphenylchlorophosphine)-decaborane was obtained from 0.6 g (0.005 M) of decaborane and 2.3 g (0.011 M) of diphenylchlorophosphine by heating in benzene. The theoretical amount of hydrogen was evolved. After 8-10 hr standing the substance crystallized from benzene. Bis-(diphenylchlorophosphine)decaborane melted with decomposition at 194-196° after recrystallization from a methylene chloride – ether mixture and then from methylene chloride. Found: Cl 12.65, 12.37%. $C_{24}H_{32}B_{10}P_2$. Calculated: Cl 12.68%.

Reaction of Triphenylarsine with Decaborane. Decaborane (0.6 g; 0.005 M) in 25 ml of toluene and 3.3 g (0.011 M) of triphenylarsine were heated until the toluene boiled. Hydrogen (120 ml) was evolved. After distilling the toluene the residue was washed several times with ether and recrystallized from methylene chloride. After two recrystallizations from methylene chloride, bis-(triphenylarsine)decaborane melted with decomposition at 152-153°. Found: B 13.96%. $C_{36}H_{12}B_{10}As_2$. Calculated: B 14.75%.

Reaction of Diacetonitriledecaborane with Triethylarsine. Diacetonitriledecaborane (1.0 g, 0.005 M) in 20 ml of benzene was heated with 2.0 g (0.012 M) of triethylarsine for 6 hr on a boiling water bath. After distilling the benzene and washing with ether, the substance was recrystallized from a methylene chloride – ether mixture. The bis-(triethylarsine)decaborane obtained melted at 140°. Found: C 32.33, 32.36; H 9.60, 9.41%. $C_{12}H_{42}B_{10}As_2$. Calculated: C 32.15; H 9.37%.

Reaction of Diacetonitriledecaborane with Diphenylchlorophosphine. As in the above experiment, bis-(diphenylchlorophosphine)decaborane was obtained from 1.0 g (0.005 M) of diacetonitriledecaborane and 2.3 g (0.011 M) of diphenylchlorophosphine in 20 ml of benzene. After two recrystallizations from a methylene chloride – ether mixture, the substance melted with decomposition at 195-197°. Found: Cl 13.37, 13.34%. $C_{24}H_{32}B_{10}Cl_2P_2$. Calculated: Cl 12.68%.

SUMMARY

1. Decaborane forms complexes of the following type: $B_{10}H_{12}(ER_3)_2$ with triethylphosphine, triethylarsine, diphenylchlorophosphine, and triphenylarsine.

2. Triethylarsine and diphenylchlorophosphine undergo an exchange reaction with diacetonitriledecaborane with formation of $B_{10}H_{12}[(C_2H_5)_3As]_2$ and $B_{10}H_{12}[(C_6H_5)_2PCl]_2$.

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REACTION OF TETRAHYDROFURAN AND TETRAHYDROPYRAN WITH TRIMETHYLBROMOSILANE AND TRIMETHYLCHLOROSILANE

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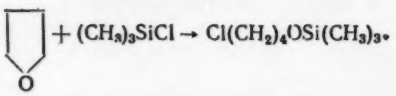
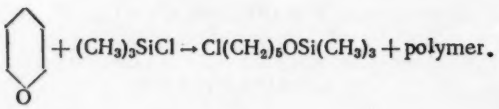
The tendency for the tetrahydrofuran ring to undergo cleavage by the action of $SiCl_4$, $RSiCl_3$, and R_2SiX_2 has been studied. Cumada and Hattori [1] showed that $C_2H_5SiCl_3$ and $(CH_3)_2SiBr_2$ form 1,4-dihalobutanes with tetrahydrofuran and 1,5-dihalopentanes with tetrahydropyran. 1,4-Dichlorobutane [2] was obtained along with polysiloxanes by heating tetrahydrofuran with dimethyldichlorosilane in the presence of aluminum chloride at 125-130°. Silicon tetrachloride in the presence of anhydrous zinc chloride cleaved tetrahydrofuran giving 1,4-dichlorobutane and di-(δ-chlorobutoxy)dichlorosilane [3]. Tetrahydro-α-methylfuran was similarly cleaved by silicon tetrachloride in the presence of anhydrous zinc chloride [4]. The main reaction product from the reaction between dimethyldichlorosilane and tetrahydrofuran in the presence of zinc chloride is 1,4-dichlorobutane. In contrast to dialkyldichlorosilanes, the reaction of tetrahydrofuran with alkyl- and aryltrichlorosilanes leads to the formation of compounds of the type $Cl(CH_2)_4OSiRCl_2$ [5].

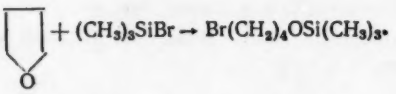
In this work we studied the reaction of tetrahydrofuran and tetrahydropyran with trimethylchlorosilane and trimethylbromosilane. It was shown that trimethylchlorosilane cleaves tetrahydrofuran only on heating in an autoclave at 160-170°; 1-chloro-4-trimethysilyloxybutane was the main reaction product:



Tetrahydropyran gave a small yield of 1-chloro-5-trimethysilyloxypentane and polymeric product upon heating with trimethylchlorosilane at 200°:



By boiling tetrahydrofuran with trimethylbromosilane (15 hr) tetrahydrofuran ring cleavage took place. It should be pointed out that the cleavage reaction also occurs at room temperature; thus, if a mixture of tetrahydrofuran and trimethylbromosilane is left for 40-45 days at room temperature, 1-bromo-4-trimethylsilyloxybutane is formed (almost quantitatively). The reaction occurs more rapidly (6 hr) in the presence of aluminum chloride, but along with 1-bromo-4-trimethylsilyloxybutane as the main reaction product a high-boiling fraction containing no silicon is also obtained:



Under these conditions, tetrahydropyran is not cleaved; ring cleavage occurs only on heating at 160-180° in a steel ampule. A mixture of 1,5-dibromopentane and 1-bromo-5-trimethylsilyloxypentane (61%:39%) is obtained as reaction product:

$+ (CH_3)_3SiBr \rightarrow Br(CH_2)_5Br + Br(CH_2)_5OSi(CH_3)_3.$

EXPERIMENTAL

Reaction of Tetrahydrofuran with Trimethylchlorosilane. Tetrahydrofuran (54 g, 0.5 M) and 55 g (0.75 M) of trimethylchlorosilane were heated in a metal ampule for 10 hr at 120-150°. The reaction product was distilled under vacuum. 1-Chloro-4-trimethylsilyloxybutane boiling at 74.5-75° (19 mm) was isolated (63.3 g, 70.0%); $n^{20}D$ 1.4270; d^{20}_4 0.9354. Found: C 46.01; H 9.43; Cl 19.82%. $C_7H_{17}SiOCl$. Calculated: C 46.51; H 9.48; Cl 19.62%.

Reaction of Tetrahydrofuran with Trimethylbromosilane. Trimethylbromosilane (24.4 g; 0.6 M) and 15 g (0.21 M) of tetrahydrofuran were heated in a flask with a reflux condenser for 15 hr. The reflux temperature gradually increased from 73 to 115°. 1-Bromo-4-trimethylsilyloxybutane was the sole reaction product; it boiled at 86-97° (17 mm); $n^{20}D$ 1.4503; d^{20}_4 1.1748; yield 33.5 g (93%). Found: C 36.98; H 7.61; Br 36.13%. $C_7H_{17}SiOBr$. Calculated: C 37.33; H 7.61; Br 35.48%.

Trimethylbromosilane (43.2 g; 0.6 M) and 61.5 g (0.4 M) of tetrahydrofuran were allowed to stand for 45 days at room temperature. Upon distillation, 1-bromo-4-trimethylsilyloxybutane boiling at 86-87° (17 mm); $n^{20}D$ 1.4502 was obtained; yield 76.5 g (91%).

Reaction of Tetrahydrofuran with Trimethylbromosilane in the Presence of Aluminum Chloride. Trimethylbromosilane (120 g; 0.78 M) and 72 g (1.0 M) of tetrahydrofuran were heated for 6 hr under a reflux condenser. The boiling point gradually rose from 73 to 115°. Two fractions were separated by vacuum distillation: I) boiling at 70° (7 mm), $n^{20}D$ 1.4503; d^{20}_4 1.1746; yield 136.6 g (71%) of 1-bromo-4-trimethylsilyloxybutane. Fraction II boiled at 137-138° (7 mm); $n^{20}D$ 1.4982; d^{20}_4 1.5000. A substance (7 ml; 10.5 g) of undetermined structure was isolated; the product contained only C, H, Br, and O, but no silicon. Found: C 34.37; H 5.55, 5.34; Br 49.27, 48.55%.

Reaction of Tetrahydropyran with Trimethylchlorosilane. Trimethylchlorosilane (10.8 g; 0.1 M) and 8.6 g (0.1 M) of tetrahydropyran were heated in a steel ampule for 12 hr at 180-200°. 1-Chloro-5-trimethylsilyloxypentane boiling at 86-89° (20 mm) was isolated (2.2 g, 12%) by vacuum distillation of the reaction products. The residue appeared to be a viscous polymeric mass. 1-Chloro-5-trimethylsilyloxypentane (2 g) was subjected to hydrolysis in 15 ml of a tetrahydrofuran–water mixture in the presence of 2-3 drops of hydrochloric acid. The reaction mixture was diluted with water, extracted with ether, and the ether solution was dried with Na_2SO_4. After distilling the ether, the residue was heated with 1.0 g of phenylisocyanate in 10 ml of toluene at 110° for 20 min. The toluene and residual phenylisocyanate were distilled under vacuum and the residue was recrystallized twice from hexane. The phenylurethane of 1-chloropentanol-5 melted at 56.7°. Found: C 59.80, 59.85; H 6.60; 6.68; Cl 14.71, 14.67; N 5.77, 5.75%. $C_{12}H_{16}O_2NCl$. Calculated: C 59.62; H 6.67; Cl 14.67; N 5.80%.

Reaction of Tetrahydropyran with Trimethylbromosilane. Tetrahydropyran (17.2 g, 0.2 M) and 30.6 g (0.2 M) of trimethylbromosilane were heated for 6 hr at 160-180° in a steel ampule. The reaction product was a mixture (61%:39%) of 1,5-dibromopentane and 1-bromo-5-trimethylsilyloxypentane according to elementary analysis; b.p. 80-82° (7 mm); 28.6 g. Found: C 34.25, 34.08; H 6.27, 6.42; Br 46.51, 46.31; Si 7.22, 7.36%.

The mixture obtained was separated by freezing from hexane (−75 to −78°). 1,5-Dibromopentane was again crystallized from a mixture of ether:hexane (1:3) at −70 to −75°. 1,5-Dibromopentane boiled at 57° (1 mm); $n^{20}D$ 1.5132; d^{20}_4 1.6967. Literature data [6]: $n^{20}D$ 1.5136; d^{20}_4 1.6995. The residue left (2.0 g) after distillation of the hexane was hydrolyzed and 1-bromobutanol-5 was identified as its phenylurethane, as described above; m.p. 60.6°. Found: C 48.35; H 5.12; Br 29.03; N 5.02%. $C_{14}H_{18}OH_2NBr$. Calculated: C 48.55; H 5.18; Br 29.36; N 5.18%.

SUMMARY

1. Trimethylbromosilane and trimethylchlorosilane cleaved tetrahydrofuran, giving 1-bromo-4-trimethylsilyloxybutane, and correspondingly, 1-chloro-4-trimethylsilyloxybutane.

2. Trimethylchlorosilane cleaves the tetrahydropyran ring, from which 1-chloro-5-trimethylsilyloxypentane and polymeric products are formed.

3. Two product, 1,5-dibromopentane and 1-bromo-5-trimethylsilyloxypentane, are obtained by cleaving tetrahydropyran with trimethylbromosilane.

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HYDROGEN ISOTOPE EFFECT IN PRIMARY ALKYL CHLORIDES IN THE PRESENCE OF APROTIC ACIDS

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It was shown in a recently published communication [1] that butyl chloride obtained by treating n-butyl chloride with deuterium chloride in a nitrobenzene solution in the presence of strong aprotic acids ($SbCl_5$, $FeCl_3$, $AlCl_3$) contained deuterium. This led to the conclusion that primary alkyl chlorides possess the ability to exchange hydrogen under the designated conditions. However, we recently discovered that different samples of n-alkyl chlorides exchanged at different rates. Thus, it was established that commercial n-butyl chloride, purified by distillation through a column of 30 theoretical plates' efficiency (b.p. 77-78°; $n^{20}D$ 1.4018; d^{20}_4 0.8858) exchanged rapidly with DCl in nitrobenzene medium with $FeCl_3$ catalysis. In contrast to this, n-butyl chloride, obtained from n-butyl alcohol by treatment with thionyl chloride, exchanged considerably more slowly in the presence of excess pyridine. Analogous results were obtained by studying the reverse hydrogen exchange reaction of deuteriobutyl chlorides, which were prepared from the corresponding deuterated alcohols. Under these conditions, the exchange rate was so low that exchange did not occur.

TABLE 1.

Fraction	B.p., °C	$n^{20}D$	IPVS, γ/ml	Content of sec-BuCl, %
I	76.5-77.0	1.4018	5835	19.20
II	77.0-77.5	1.4019	4340	4.85
III	77.5-77.5	1.4019	2360	4.00
IV	77.5-77.5	1.4020	1485	0.75
V	77.5-77.5	1.4020	183	0
VI	77.5-77.5	1.4020	83	0

TABLE 2.

Fraction	B.p., °C	$n^{20}D$	IPVS, γ/ml	Content of sec-propyl chloride, %
I	43.5-45	1.3875	7000	15.9
II	45 -46	1.3880	3640	6.00
III	46 -46.1	1.3885	1642	1.80
IV	46.1	1.3885	560	0.54
V	46.1	1.3884	190	0.13
VI	Residue	1.3885	183	0.01

In order to explain the phenomena observed above, we attempted careful examination of the purity of charged and isolated materials by gas chromatographic methods. These studies, carried out on a dioctyl phthalate (20 wt-% on C-22 firebrick) column 2 m in length, showed that the n-butyl chloride we synthesized, and the deuterated n-butyl chloride were pure substances, but that the chloride obtained by distilling a commercial preparation contained 0.1-0.2% of admixed sec-butyl chloride. Moreover, it was shown that, in all cases in which hydrogen exchange was observed, isomerization of n-butyl chloride to secondary, the content of which was about 1% of the butyl chloride isolated after the reaction, occurred. The hydrogen exchange reaction of chromatographically pure n-butyl chloride

with DCl in the presence of $FeCl_3$ at 20° led to butyl chloride with a considerable deuterium content. However, by careful distillation of this product through a column with subsequent analysis of the different fractions for deuterium content and sec-butyl chloride content, it was shown that the apparent hydrogen exchange for n-butyl chloride is dependent on the presence of easily exchanging sec-butyl chloride, which is formed from n-butyl chloride by isomerization. The fraction corresponding to pure n-butyl chloride contains practically no deuterium. Similar results were obtained in work with commercial n-butyl chloride purified by distillation through a column of 30 theoretical plates' efficiency. Also, in this case, the fraction of gas-chromatographically pure n-butyl chloride contained almost no deuterium (Table 1), although the distilled reaction product contained considerable deuterium (IPVS* = 1335 γ/ml).

These results seemed direct proof that apparent hydrogen exchange in n-butyl chloride requires the presence of sec-butyl chloride which is formed as a result of isomerization or is present as an impurity in the starting material. This supposition was confirmed by studying hydrogen exchange of chromatographically pure n-propyl chloride which we synthesized from n-propyl alcohol and thionyl chloride in the presence of pyridine (b.p. 45.8°; $n^{20}D$ 1.3886; d^{20}_4 0.8924). As a result of hydrogen exchange of n-propyl chloride in nitrobenzene with DCl in the presence of $SbCl_5$ (ratios of components: n-PrCl:nitrobenzene:$SbCl_5$:DCl = 1:9.2:0.16:0.4) at 25° for 16 hr, a product containing considerable deuterium (IPVS = 2000 γ/ ml) was isolated. However, as was shown by subsequent fractionation, gas chromatographic, and isotopic analyses, hydrogen exchange in this case also required the presence of sec-propyl chloride, but n-propyl chloride contained practically no deuterium (Table 2).

Finally, we studied the hydrogen exchange reaction of ethyl chloride, which generally is incapable of isomerizing to a sec-chloride, and established that ethyl chloride does not undergo hydrogen exchange with deuterium chloride in nitrobenzene solution in the presence of aprotic acids ($FeCl_3$, $SbCl_5$).

Thus, the results obtained show that in the absence of tert- or sec-alkyl chlorides, n-alkyl chlorides do not undergo hydrogen exchange with deuterium chloride in nitrobenzene solution even in the presence of strong aprotic acids. Hydrogen exchange observed under these conditions depends on the formation of sec-alkyl chlorides.

SUMMARY

Based on n-butyl, n-propyl, and ethyl chlorides as examples, it was established that these alkyl chlorides, in the absence of tert- or sec-alkyl chlorides, do not undergo hydrogen exchange reaction with deuterium chloride in nitrobenzene solution in the presence of aprotic acids. Under these conditions, n-BuCl and n-PrCl are isomerized to secondary alkyl chlorides, which easily undergo the hydrogen exchange reaction.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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*IPVS - excess density of water, obtained by combustion of the chloride.

REACTION OF DECABORANE AND PENTABORANE WITH MERCAPTANS AND SULFIDES

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A detailed study of the cleavage of decaborane by alcohols with various structures [1,2] was made. It was found that the reaction occurs according to the equation

$$B_{10}H_{14} + 30ROH \rightarrow 10B(OR)_3 + 22H_2.$$

Pentaborane behaves similarly with reference to alcohols. Trialkoxyborane and H_2 [3] are formed quantitatively by reaction of pentaborane with methyl, ethyl, or butyl alcohols:

$$B_5H_9 + 15ROH \rightarrow 5B(OR)_3 + 12H_2.$$

In the present work we studied the reaction of decaborane and pentaborane with mercaptans. It was shown that decaborane and pentaborane are much more stable to mercaptans than to alcohols. Reaction did not occur during prolonged heating of decaborane with ethyl mercaptan at its boiling point; only at 150-160° did cleavage of decaborane with formation of hydrogen and tri(thioethyl)boron occur according to the equation

$$B_{10}H_{14} + 30C_2H_5SH \rightarrow 10B(SC_2H_5)_3 + 22H_2.$$

Butyl mercaptan began to react with decaborane at temperatures above 120° although the complete cleavage reaction required heating for 60 hr:

$$B_{10}H_{14} + 30C_4H_9SH \rightarrow 10B(SC_2H_5)_3 + 22H_2.$$

The reaction of pentaborane with ethyl mercaptan at the boiling point of the mixture occured slowly, and only about $^2/_3$ of the theoretical amount of hydrogen was evolved. Apparently, pentaborane forms a complex compound with ethyl mercaptan, since tri-(thioethyl)boron is not distilled from the reaction mixture under a vacuum of 1 mm, even at 150°. But tri-(thioethyl)boron was obtained by thermal decomposition (at 200°) of the complex formed. Similarly, tri-(thiobutyl)boron is the final product from the reaction of pentaborane with butyl mercaptan:

$$B_5H_9 + 15C_4H_9SH \rightarrow 5B(SC_4H_9)_3 + 12H_2.$$

Besides the above mercaptans, we studied the reaction between decaborane and diethyl- and diphenylsulfides. It was shown that diethylsulfide and decaborane react with formation of a complex $B_{10}H_{32}C_8S_2$ in composition and hydrogen evolution; apparently this complex is analogous to those of decaborane with triethylamine, triphenylphosphine, acetonitrile, etc. [4-7]:

$$B_{10}H_{14} + (C_2H_5)_2\ S \rightarrow B_{10}H_{12}[(C_2H_5)_2S]_2 + H_2.$$

Diphenylsulfide did not undergo this reaction with decaborane on heating in either benzene or toluene.

EXPERIMENTAL

Reaction of Pentaborane with Ethyl Mercaptan. Pentaborane (0.64 g; 0.01 M) and 9.5 g (0.15 M) of ethyl mercaptan were mixed under an argon atmosphere. No visible indications of reaction were observed, and slow evolution of hydrogen commenced only upon boiling the mixture (12 hr). After distillation of excess ethyl mercaptan the residue was distilled under vacuum to 180-200° at which 0.8 g of tri-(thioethyl)boron was distilled; b.p. 68-70° (1.5 mm); $n^{20}D$ 1.5457.

Reaction of Pentaborane with Butyl Mercaptan. To butyl mercaptan (13.5 g; 0.15 M) heated to the boiling point was slowly added pentaborane (0.64 g; 0.01 M). Tri-(thiobutyl)boron (13 g) was obtained by heating the reaction mixture under vacuum; yield 94.5%; b.p. 152-153° (1 mm); $n^{20}D$ 1.5230; d^{20}_4 0.9864.

Reaction of Ethyl Mercaptan with Decaborane. Decaborane (0.6 g; 0.005 M) and 10 g (0.16 M) of ethyl mercaptan were heated in an autoclave at 160-180° for 12 hr. The hydrogen evolved was collected in a gasometer (2.7 liters). The residue boiled at 132-133° (22 mm) upon distillation. After a second distillation, tri-(thioethyl)boron boiled at 131° (21 mm); $n^{20}D$ 1.5480; d^{20}_4 1.0386. Found: B 5.70; C 37.19; H 7.66%. $C_6H_{15}S_3B$. Calculated: B 5.67; C 37.12; H 7.73%.

Reaction of Butyl Mercaptan with Decaborane. Decaborane (0.6 g; 0.005 M) and butyl mercaptan were heated in a flask with reflux condenser. Butyl mercaptan was added in small portions (about 3 ml) as the boiling point increased. The temperature gradually increased from 120 to 160°. Heating was continued approximately 60 hr. The theoretical amount of hydrogen was evolved. The residue was distilled under vacuum. After a second distillation, tri-(thiobutyl)boron boiled at 207° (22 mm); $n^{20}D$ 1.5205; d^{20}_4 0.9686. Literature data [8]: b.p. 150-152° (1 mm); $n^{20}D$ 1.5205; d^{20}_4 0.9684. Found: B 3.88; C 51.90; H 9.73%. $C_{12}H_{27}S_3B$. Calculated: B 3.92; C 51.83; H 9.72%.

Reaction of Decaborane with Diethylsulfide. A solution of 0.6 g (0.005 M) of decaborane and 2.3 g (0.015 M) of diethylsulfide in 20 ml of benzene was heated on a boiling water bath in a flask with a reflux condenser. The theoretical amount of hydrogen (120 ml) was evolved. The benzene was distilled, and the residue was washed twice with ether to remove excess diethylsulfide. Bis-(diethylsulfide)decaborane melted at 89-90° after three crystallizations from a methylene chloride – ether mixture. Found: C 31.95, 31.99; H 10.74, 10.80%. $C_8H_{32}B_{10}S_2$. Calculated: C 32.00; H 10.67%.

Diphenylsulfide did not react with decaborane under similar conditions; the results were the same in toluene.

SUMMARY

1. Reaction of decaborane and pentaborane with ethyl and butyl mercaptans led to cleavage and hydrogen evolution with formation of corresponding thioalkyl borates.

2. Diethylsulfide formed the complex $B_{10}H_{12}[(C_2H_5)_2S]_2$ with decaborane.

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SYNTHESIS OF SOME DIALKYLAMINE-BORANES AND ALKYLMERCAPTO-(DIALKYLAMINO) BORANES

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We recently reported some new boron derivatives in which the boron atom is bound to three different substituents: alkylmercapto- and dialkylamino- groups and a hydrogen atom [1,2]. The first examples of this type of compound were obtained by us by reacting mercaptans with a borane-diethyl amine complex at 100-120°. This reaction, as was shown, has a general character which allows synthesis of various alkylmercapto-(dialkylamino) boranes from borane complexes with secondary amines.

The dialkylamine-borane used (1) can be obtained readily by passing diborane into an ethereal solution of the corresponding secondary amine. We previously synthesized diethylamine-borane [1] by this route and dimethylamine-borane, diisoamylamine-borane, and piperidine-borane in yields close to theoretical in the present work. Dimethylamine-borane was previously obtained from diborane and dimethylamine in the gaseous phase [3]; Berg and Good [4] obtained complexes with boron and cyclic amines, in particular with piperidine, by this same route but did not describe their properties. A convenient synthetic method for dialkylamine-boranes consists of the reaction of lithium borohydride with amine hydrochlorides in ethereal medium [5]. By reaction of the corresponding mercaptans at 100 to 120° on dimethylamine-borane, diisoamylamine-borane, or piperidine-borane we synthesized n-propylmercapto-(dimethylamino)-borane, n-butylmercapto-(dimethylamino)-borane, n-propylmercapto-(diisoamylamino) borane, and n-butylmercapto-(piperidino)-borane in 70-80% yields, according to the equation

$$R_2NH \cdot BH_3 + R'SH \longrightarrow R_2NB\begin{matrix}SR'\\H\end{matrix} + 2H_2.$$

The alkylmercapto-(dialkylamino) boranes exist in monomeric form; they are hydrolyzed and oxidized in air and react with alcohols at room temperature with hydrogen evolution. Replacement of the alkylmercapto group by alkylamino- or dialkylamino-groups occurs upon reaction with primary or secondary amines. The alkylmercapto-(dialkylamino) boranes exchange the RS-group for a higher alkylmercapto group by heating with a higher mercaptan. Replacement of alkylmercapto- and dialkylamino- groups occurs on heating with an excess of higher secondary amine.

The IR- and Raman-spectra of the different alkylmercapto-(dialkylamino) boranes were studied. Data for n-butylmercapto-(dimethylamino) borane are given:

IR-spectra (cm^{-1}): 817 (20); 870 (84); 882 (87); 925 (89); 964 (86); 1004 (95); 1070 (54); 1147 (3); 1226 (17); 1279 (67); 1298 (71); 1382 (69); 1410 (1); 1455 (27); 1513 (15); 2371 (71); 2500 (39); 2862 (19); 2875 (22); 2980 (4); 2960 (10).

Raman-spectra (cm^{-1}): 346 (1); 376 (1); 465 (2); 663 (7); 715 (2); 742 (3); 773 (1); 808 (3b); 870 (5); 895 (1); 925 (0); 969 (0); 997 (0); 1016 (0); 1056 (6); 1101 (3); 1144 (5); 1194 (0); 1228 (1); 1276 (2); 1302 (3); 1354 (3b); 1379 (0); 1408 (10); 1446 (8); 1458 (1); 1506 (0); 1629 (0).

EXPERIMENTAL

Dimethylamine-borane. To a solution of 15.0 g (0.333 M) of dimethylamine in 100 ml of absolute ether was added 0.21 M of diborane at −20 to −10°, after which the ether was distilled. Dimethylamine-borane obtained as a liquid crystallized on standing; yield 18.9 g (96%). Dimethylamine-borane was purified by distillation under vacuum.

Diisoamylamine-borane. Diisoamylamine (31.4 g, 0.2 M) was dissolved in 120 ml of absolute ether; to it was added 0.125 M of diborane at 0°; then the ether was distilled, and the crystalline residue of diisoamylamine-borane was washed with hexane. The yield was 33.2 g (97%). After recrystallization from hexane, diisoamylamine-borane melted at 54-56°. Found: C 69.88, 69.60; H 15.35, 15.22; B 6.59, 6.68%. $C_{10}H_{26}NB$. Calculated: C 70.18; H 15.32; B 6.32%.

Piperidine-borane. Diborane (0.14 M) was added to a solution of 21.2 g (0.25 M) of piperidine in 75 ml of ether. After distillation of ether under vacuum 24.0 g (97%) of piperidine-borane was obtained as colorless crystals melting at 80-82° after recrystallization from a mixture of hexane and benzene. Found: C 60.55, 50.51; H 14.28, 14.35; H_{act} 3.12%. $C_5H_{14}NB$. Calculated: C 60.57; H 14.25; H_{act} 3.06%.

Piperidine-borane and diisoamylamine-borane are crystalline substances with marked, rapid decomposition above 130°. Piperidine-borane is soluble in benzene and ether, less soluble in n-hexane. Diisoamylamine-borane is very soluble in benzene, as well as in ether and in n-hexane.

n-Propylmercapto-(dimethylamino) Borane. In a three-necked flask equipped with a long-stem thermometer, reflux condenser, and dropping funnel were charged 9.5 g (0.161 M) of dimethylamine-borane and 6.0 g of n-propyl mercaptan. The mixture was heated while 7.4 g more of n-propyl mercaptan was added in drops while the temperature of the reaction mixture was held in the range 100-120°. After 2.5 hr hydrogen evolution stopped. n-Propylmercapto-(dimethylamino) borane (14.8 g; 70%), boiling at 48-50° (13 mm), was obtained by fractional distillation; d^{20}_4 0.8706; $n^{20}D$ 1.4701. Found: C 46.37, 46.43; H 10.62, 10.64%; mol. wt. 134.9. $C_5H_{14}NSB$. Calculated: C 45.82; H 10.76%; mol. wt. 131.1.

n-Butylmercapto-(dimethylamino) Borane. A mixture of 10.6 g (0.180 M) of dimethylamine-borane and 16.7 g (0.185 g) of n-butyl mercaptan were heated for 2 hr at 100-120°. After fractional distillation 19.5 g (75%) of n-butylmercapto-(dimethylamino)-borane boiling at 55-57° (7 mm) was obtained; d^{20}_4 0.8666; $n^{20}D$ 1.4699. Found: C 49.72, H 11.14%. $C_6H_{16}NSB$. Calculated: C 49.63; H 11.11%.

n-Propylmercapto-(diisoamylamino) Borane. To 22.4 g (0.131 M) of diisoamylamine-borane was added 5.2 ml of propyl mercaptan; 4.9 g more of n-propyl mercaptan was added dropwise during heating at 100-120°. After hydrogen evolution stopped, the mixture was fractionally distilled. n-Propylmercapto-(diisoamylamino) borane (25.0 g; 79%) boiling at 110-114° (3.5 mm) was obtained; after a second distillation it boiled at 92-94° (1.5 mm); d^{20}_4 0.8422; $n^{20}D$ 1.4640. Found: C 64.25, 64.40; H 12.57, 12.27%; mol. wt. 237.0. $C_{13}H_{30}NSB$. Calculated: C 64.15; H 12.43; mol. wt. 243.3.

n-Butylmercapto-(piperidino) Borane. A mixture of 9.4 g (0.095 M) of piperidine-borane and 9.0 g (0.1 M) of n-butyl mercaptan were heated at 100-120° for 3 hr. After distillation, 14.4 g (82%) of n-butylmercapto-(piperidino) borane boiling at 73-74° (1.5 mm) was obtained; d^{20}_4 0.9170; $n^{20}D$ 1.4944. Found: C 58.39, 58.13; H 10.63, 10.89; S 17.08%; mol. wt. 184.9. $C_9H_{20}NSB$. Calculated: C 58.39; H 10.89; S 17.32%; mol. wt. 185.1.

Crystalline substances, not further studied, were obtained as impurities in these experiments for obtaining alkylmercapto-(dialkylamino) boranes.

SUMMARY

1. Borane complexes with dialkylamines can be prepared in almost quantitative yields by addition of diborane to ethereal solutions of the corresponding amines.

2. Alkylmercapto-(dialkylamino) boranes are obtained in good yields by the reaction of mercaptans with complexes of borane and secondary amines at 100-120°.

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REACTION OF TETRAHYDROSILVANE AND SILVANE WITH SULFUR

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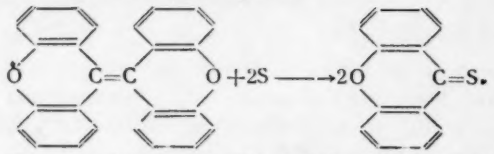
It is well known that elementary sulfur is a very active chemical reagent. This property of sulfur is used in industrial chemistry, as in vulcanization of rubber, as well as in organic syntheses. Work on the reaction of sulfur with hydrocarbons is well known [1]. Dehydrogenation products are the main products of this reaction: olefins, hydrogen sulfide, and thiophene. The reaction between sulfur and other organic compounds has as yet been studied incompletely. Upon reaction of sulfur with such heterocyclic compounds as dixanthylene and diflavylene at 280° and atmospheric pressure, cleavage of the ethylenic bond occurs but the ethereal oxygen remains unaffected [2]. For example, the reaction goes according to the scheme, in the case of dixanthylene:



We investigated the reaction between elementary sulfur and the oxygen heterocyclic compounds tetrahydrosilvane and silvane. The experiments were conducted in a steel autoclave. The reaction products were analyzed on a gas–liquid chromatography column packed with diatomaceous earth impregnated with tricresyl phosphate (30%). The column was 2 m long. Analysis was conducted at 80°; the hydrogen flow rate was 30 ml/min and the pressure 0.2 atm. By distilling the reaction products between tetrahydrosilvane and sulfur through a column with an efficiency of 20 theoretical plates, the following were isolated: α-methylthiophene, b.p. 112-113° (751 mm); $n^{20}D$ 1.5120 and d^{20}_4 1.0170; α-methylthiophane, b.p. 131-132° (751 mm); $n^{20}D$ 1.4920 and d^{20}_4 0.9581; silvane, b.p. 63-64° (751 mm); $n^{20}D$ 1.4340 and d^{20}_4 0.9154, and pentanone-2, b.p. 100-101° (751 mm); $n^{20}D$ 1.3916 and d^{20}_4 0.8083. The conditions for conducting, and the results of, the experiments are given in Tables 1 and 2.

TABLE 1. Reaction of Sulfur with Tetrahydrosilvane (in each experiment 100 g of tetrahydrosilvane and 40.4 g of sulfur were taken)

Experimental conditions			Results of experiments			
temperature of experiment, °C	initial N_2 pressure, atm	length of experiment, hr	yield of liquid products, g	amount of tetrahydrosilvane reacting, %	yield of methylthiophene, mole-% on react. tetrahydrosilvane	yield of methylthiophane, mole-% on react. tetrahydrosilvane
150••	Without excess pressure	12	91.9	–	–	–
200	The same	6	123.3	52.2	8.7	–
200	20	6	126.5	67.3	17.8	11.3
200	50	6	127.8	62.7	8.8	2.5
200•	20	12	164.1	66.8	39.5	13.1
250	20	10	119.9	77.8	31.0	7.7
250••	20	10	108.0	42.0	15.0	–

•In this experiment, 129 g of tetrahydrosilvane and 52.0 g of sulfur were used.
••In this experiment, 100 g of tetrahydrosilvane and 20.2 g of sulfur were used.

TABLE 2. Reaction of Sulfur with Silvane (in each experiment 100 g of silvane and 42.3 g of sulfur were taken)

Experimental conditions			Results of experiment			
experimental temp., °C	length of experiment, hr	initial N_2 pressure, atm	yields of liquid products, g	amt. of silvane converted, %	yield of methylthiophene, mole-% on reacting silvane	yield of methylthiophene, mole-% on initial silvane
150	12	no excess pressure	95.5	17.2	0	0
200	12		72.4	70.6	9.2	6.5
250	12		66.7	98.6	13.5	13.3
250	6		74.8	95.4	13.0	13.0
250			68.7	88.8	10.5	9.3
300	6		68.4	81.7	15.1	10.8
300	4		63.2	78.7	8.9	7.0
300	4	25	62.4	97.6	4.9	4.8

As is seen from Tables 1 and 2, the reaction for replacing an atom of oxygen by sulfur goes at temperatures above 150°. Thus, from tetrahydrosilvane and sulfur, α-methylthiophene and α-methylthiophane are obtained, but α-methylthiophene from silvane and sulfur. The influence of changing the temperature, duration of the experiment, and nitrogen pressure on the yield of sulfur heterocyclic compounds was studied. During reaction between sulfur and tetrahydrosilvane within the limits we investigated, increasing the temperature or reaction time led to increased yields of α-methylthiophene and α-methylthiophane. Better yields of sulfur heterocycles were obtained at initial pressures of about 20 atm. The yield of α-methylthiophene was considerably lower from the reaction of sulfur with silvane than from the reaction of sulfur with tetrahydrosilvane. The maximum yield of α-methylthiophene did not exceed 15.1% of reacting silvane. Here, apparently, the polymerization of silvane limits the reaction. Therefore, increasing temperature, pressure, or reaction time increases the amount of high-boiling products while the yield of α-methylthiophene is essentially unchanged.

Since α-methylthiophene is formed as a main product from tetrahydrosilvane and sulfur, it is suggested that initially formed α-methylthiophane undergoes dehydrogenation by sulfur to α-methylthiophene. Sulfur dehydrogenation to silvane under these same conditions was conducted for the same starting tetrahydrosilvane. The silvane content in the condensate from one of the experiments was 22.6%.

Furthermore, part of the tetrahydrosilvane is isomerized into pentanone-2 under our experimental conditions. However, the main portion of the tetrahydrosilvane and silvane conversion products are high-boiling substances which, apparently, are "linkage" products of molecular sulfur with tetrahydrosilvane, silvane, and methylthiophene into larger molecules as during the vulcanization of rubber. In the case of silvane, polymerization also occurs.

The mechanism for forming methylthiophene from tetrahydrosilvane and silvane is not yet clear. The supposition of direct displacement of the oxygen atom by sulfur has not been established experimentally, since it was not possible to detect sulfur in gaseous oxygen compounds. Consequently, the idea is not excluded that α-methylthiophene and α-methylthiophane are formed as a result of reaction between silvane and tetrahydrosilvane with hydrogen sulfide, which is detected in considerable amounts among the reaction products. However, hydrogen sulfide, as shown in a separate experiment, does not react with tetrahydrosilvane or silvane under the conditions we used. Experiments conducted to clarify the action of sulfur on tetrahydrosilvane in the presence of hydrogen sulfide showed that the latter has no influence on the yield of sulfur heterocyclic compounds. Use of aluminum oxide as a catalyst also did not have an effect on the reaction course.

SUMMARY

During direct reaction of sulfur with tetrahydrosilvane and also with silvane at 200-250° and 20 atm pressure, α-methylthiophane and α-methylthiophene are formed; higher yields are obtained by the reaction of sulfur with tetrahydrosilvane. Under optimum conditions the total yield of methylthiophene and methylthiophane is 52.6%, calculated on reacting tetrahydrosilvane.

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VOLUMETRIC TERMINATION IN MICRO DETERMINATION OF CARBON AND HYDROGEN AFTER DECOMPOSITION OF ORGANIC SUBSTANCES BY COMBUSTION IN A STREAM OF OXYGEN

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The tendency noted by Lindner to reject terminal weighing in determining carbon and hydrogen in elementary analysis, opening the possibility for almost completely automatic processes, has recently made some progress. Titrometric [1-3], manometric [4,5], and conductometric [6,7] endpoints for determining carbon and hydrogen were presented. In the largest number of methods, water formed by combustion of organic compounds is converted to an easily determined form. A number of preparations of HCl, HBr, NH_3, and C_2H_2 from water were studied. But none of them was completely satisfactory. The halogen-containing preparations [1, 8-11] were either too volatile, or they reacted with water too slowly. CaC_2, which Malissa used, decomposed rapidly. We tried (apparatus, Fig. 1) a series of halo derivatives of organosilicon, phosphorus, and boron compounds and found that of the compounds we investigated only phenylborondichloride [12] was usable as a reagent under our conditions (Table 1); it formed HCl from water rapidly and quantitatively, and was only slightly volatile.

TABLE 1.

Preparation	Physical properties	Value for blank in ml of 0.05 N caustic	Oxygen flow rate, ml/min	Amount of oxygen passed, ml	Amount of water converted to hydrochloric acid, %
γ-Chlorobutyoxyphenyldichlorosilane	Liquid, b.p. 136° (8 mm)	0.05	25	1000	46.60
		0.04	8.3	1000	52.45
Diphenyldichlorosilane	Liquid, b.p. 175° (18 mm)	0.08	15	1000	45.84
		0.08	30	1000	40.00
γ-Chlorobutoxydichlorophosphine	Liquid, b.p. 80° (5 mm)	1.9	48	500	35.5
		1.73	48	1000	43.23
Diethyl-α-chloroethylchlorosilane	Liquid, b.p. 154-155° (15 mm)	0.04	50	1000	20.80
		0.04	50	1000	24.00
		0.44	27	500	44.30
Bromomethyltrichlorosilane	Liquid	1.10	27	500	42.00
Bis-trichlorosilylchloromethane	Liquid, b.p. 211°	0.05	30	1000	56.40
		0.06	45	1000	46.20
1,2,3,4,7,7-Hexachlorobicyclo(2,2,1,2-heptenyl-6β-ethyltrichlorosilane)	Viscous mass	0.02	30	1000	74.00
		0.02	30	500	51.80
Dinaphthylboronchloride	Solid substance	0.05	40	500	26.00
		0.03	20	500	46.00
Diphenylboronchloride	Liquid, b.p. 119-120° (3 mm)	0.06	30	1000	74.00
		0.05	15	1000	80.00
Phenylborondichloride	Liquid, b.p. 175°	0.12	40	500	100.30
		0.30	40	500	100.20

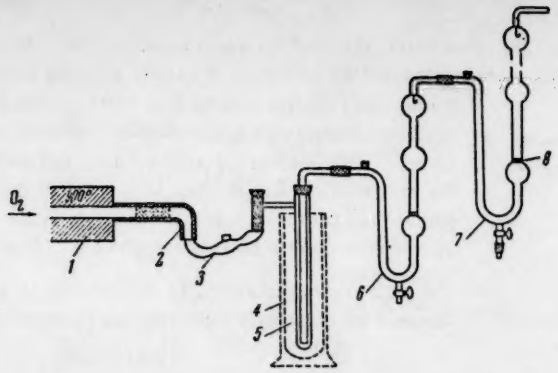

Fig. 1. Apparatus for converting H_2O to HCl and absorption of HCl and CO_2: 1) combustion tube; 2) iron block, the end of which is in furnace (900°); 3) apparatus with phenylborondichloride; 4) Dewar flask; 5) trap; 6), 7) absorption apparatus; 8) glass filter porosity No. 3.

TABLE 2.

Substance	Weight, mg	Amount, ml		C, %			H, %		
		0.05N caustic, consumed in neutraliz. HCl	0.025N NaOH, consumed neutralizing CO_2	found	calc.	diff.	found	calc.	diff.
Naphthalene	5,448	6,72	34,02	93,67	93,75	0,08	6,17	6,27	0,10
	5,419	6,59	34,00	94,11		0,36	6,20		0,07
Octadiyne-3,5-diol-2,7	4,698	6,46	21,798	69,61	69,54	0,07	7,41	7,30	0,11
18-Nor-D-homo-$\Delta^{(9,11)}$-3,15,17a-triacetoxyandrostene	5,284	8,11	24,558	69,72		0,18	7,67		0,37
	4,765	7,43	22,04	69,38	69,20	0,18	7,80	7,74	0,06
	4,750	7,40	21,96	69,36		0,16	7,79		0,05
Dimethyl ester of 7-methoxy-1,2,3,4, 4a,9,10,10a-octahydrophenanthrene-1,2-dicarboxylic acid	4,860	7,16	22,24	68,64	68,66	0,02	7,37	7,23	0,14
	5,493	8,23	25,04	68,38		0,28	7,49		0,26

It was difficult to determine the equivalent point during titration with soda in various solvents. Consequently, we absorbed HCl and CO_2 separately in distilled water and caustic, respectively. Absorption of CO_2 in 0.2 N NaOH was incomplete (10 ml of solution rose 6 cm) under our conditions. With 0.1 N solution of $Ba(OH)_2$ we had difficulty, connected with the quantitative removal of the residue of $BaCO_3$ which is insoluble in water. Alcoholic NaOH solution (0.075 N) was somewhat better and quantitatively absorbed CO_2, and the precipitated residue of sodium carbonate was easily washed into the titration vessel with water. In order to avoid determining excess caustic in the presence of soda, a solution of barium chloride was added throughout the titration. In the blank experiment a liter of oxygen (30-35 ml/min) was passed through the vessel. HCl, formed due to the volatility of phenylborondichloride, was absorbed in distilled water and titrated with 0.05 N caustic solution, the amount of which did not exceed 0.1-0.3 ml. To the alcoholic caustic (10 ml of 0.075 N solution) was added 20 ml of 20% $BaCl_2$ solution, and after 20 min mixing the solution was titrated with hydrochloric acid. In order to accelerate the titration, 5 ml of 0.1 N HCl was added to the solution with a calibrated pipet at the beginning; then it was titrated with 0.025 N HCl (blank experiment for CO_2). The value for the blank experiment was sufficiently constant for 2 or 3 determinations if the absorption apparatus was rinsed with dilute acid and then with water. A weighed sample of 5-7 mg was placed in the combustion tube and burned with a spark [13,14] in a stream of oxygen (30-35 ml/min; for combustion displacement of 1 liter of oxygen was used). The mixture of gases formed was passed through the apparatus with phenylborondichloride, then through the trap cooled with dry ice, and through the two absorption vessels.

HCl was absorbed by the distilled water, the solution was transferred into a flask and titrated with 0.05 N caustic solution in the presence of phenolphthalein. 1.0 ml of 0.0005 N caustic solution corresponds to 0.0005 mg of hydrogen. Carbon dioxide was absorbed in 0.075 N alcoholic NaOH solution (10 ml, as in the blank experiment); the solution was transferred to the titration vessel (Fig. 2), 20 ml of 20% barium chloride solution was added, and after 20 min stirring, the excess alkali was titrated with 0.025 N HCl in the presence of ortho-cresolphthalein. 1.0 ml of 0.025 N caustic is equivalent to 0.0015 mg of carbon. The sample determinations are given in Table 2.

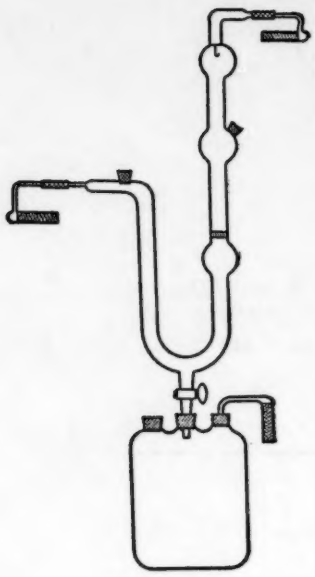

Fig. 2. Absorption apparatus and titration vessel.

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SUMMARY

1. Halogen-containing organo-B, -P, and -Si compounds were used as preparations reacting with water vapor to form HCl for volumetric determination of hydrogen in organic compounds.

2. The possibility of volumetric micro-determination of carbon and hydrogen in organic substances after combusting them in a stream of oxygen in a tube mixed with phenylborondichloride, which forms hydrogen chloride with water vapor, was demonstrated.

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HEAT CONDUCTION OF 2,4,6-TRINITROTOLUENE IN THE SOLID AND LIQUID STATES

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In recent years a number of studies have been published on the heat conductivity of organic compounds of very different structures, both in the solid and the liquid state. In particular, there have been many studies of the temperature dependence of the heat conduction of liquid organic compounds and the effect of molecular structure on the numerical value of the heat conduction [1]. Considerably fewer works have been devoted to the question, interesting from both a scientific and practical point of view, of the change in heat conductivity as a result of phase transformation. In this connection, we note the work of Read and Lloyd [2], which reports a study of the heat conduction of 2,4,6-trinitrotoluene (trotyl) in the temperature range from 20-120°, carried out by the method of heated fibers. The authors found that the heat conductivity of trotyl decreased evenly from 20 to 75-77°; the section ab of Curve 1 (Fig. 1) in the graph of Read and Lloyd. Here the value of the heat conductivity in the solid state changed from $37 \cdot 10^{-5}$ to $32 \cdot 10^{-5}$ cal/ cm · sec · degree. Beginning from 71-72°, there was a sharp fall in heat conduction to the value $3 \cdot 10^{-5}$ cal/ cm · sec · degree (section bc of Curve 1), then there was some exponential rise of the curve to point d, corresponding to about 100°, after which the portion of curve de practically paralleled the abscissa. The section of the curve cde corresponds to the liquid state (the melting point of the trotyl used by Read and Lloyd was 80.4°).

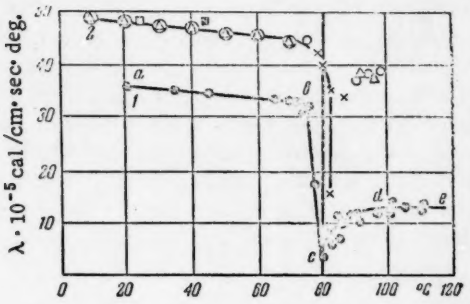

Fig. 1. Heat conductivity of 2,4,6-trinitrotoluene in solid and liquid states: ○, △, × – our data; ■ – data of A. F. Belyaev; ● – data of Read and Lloyd.

We could find values in the literature for the heat conduction of trotyl only for 25 and 45° [3,4]. Even with a rapid consideration of the data obtained by the English authors, we note the fact that the values for the heat conduction of 2,4,6-trinitrotoluene at 25 and 45° differ sharply from the values of heat conduction of trotyl obtained by other investigators for these same temperatures. Also, there is great interest in the question of the reproducibility in the zone of the melting point of the minimum in the heat-conduction curve when using studies by other methods for measuring the heat-conduction coefficient; of the origin of this minimum, and also the absolute values for the heat conduction of trotyl in solid and liquid states. In accord with this, we have measured the heat conduction of a number of samples of pure 2,4,6-trinitrotoluene in the temperature range from 10-96°.

EXPERIMENTAL

The heat conduction in the solid and liquid state, and also over the melting point range was studied in an apparatus based on the principle of comparative measurement of the heat conduction of thin, flat layers of substance under conditions of stationary heat flow. This method, often used by many investigators [5-7], was used by us in an apparatus which permitted us to take as a minimum amount of substance for study, about 1-1,5 g. The diagram of the apparatus is shown in Fig. 2, where the numbers 1 and 3 denote the thermostatically controlled blocks used to create a constant temperature difference between the surfaces of the thin (0,5-1 mm) layer of substance studied. Due to the choice of such a thin layer and heating from above, we avoided convection. The heat loss into the surrounding

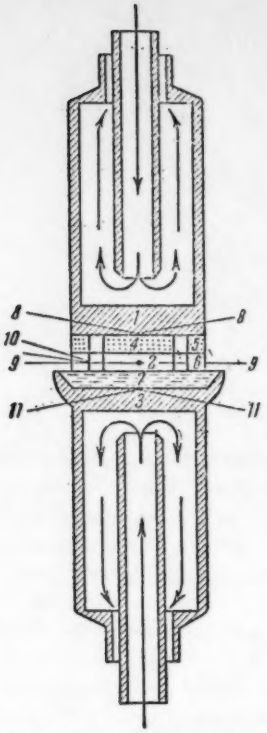

Fig. 2. Apparatus for determining heat conduction by the relative method of flat layers: 1) upper block; 2) middle block; 3) lower block; 4) standard sample; 5) protective ring for the standard material; 6) copper protective ring; 7) substance under investigation; 8) thermocouple for upper block; 9) thermocouple for middle block; 10) thermocouple for copper protective ring; 11) thermocouple for lower block.

medium at the temperatures measured, because of the presence of the special protective rings 5 and 6, was slight (on the order of 1%), and the experimental error did not exceed 2%. As the standard substance we chose water, glycerol, toluene, air, whose heat conductions have been well studied by many investigators.

Our experimental results are given in Fig. 1 (Curve 2); the sign ○ denotes the points taken on shifting from a low temperature (10°) to a high one (98°); the sign △ means in the reverse direction. A consideration of Curve 2 shows that these results fit well on the curve which we give and agree within the limits of error of the experiment. Also, the values for the heat conduction of trotyl at 25 and 45° obtained by Prentiss [3] and Belyaev [4] agree well with our results. Curve 2 as a whole reproduces well the general character of Curve 1 (Read and Lloyd) and agrees, in particular, with the same temperature coefficient of heat conduction as the English authors, but our values for the heat conduction of trotyl are considerably higher. In particular, a sharp difference occurs in the region of the heat conduction of liquid trotyl, where the difference reaches about 200%. The data of Read and Lloyd on the heat conduction of liquid trotyl are very perplexing where they approach the value of the heat conduction of air. We are inclined to assume that, in the studies of the English authors, there was some systematic error which lowered the heat conduction, and was shown especially obviously in measuring the heat conduction of the fused trotyl.

The minimum on the heat-conduction curve of trotyl close to the melting point, which we could reproduce only under definite experimental conditions (see sign × in Curve 2), can be explained by noting that this effect is not related to lowering of the heat conduction of the solid substance before the melting point, but at temperatures close to melting part of the heat is used in maintaining a definite layer of substance in the fused state. This is confirmed by the fact that the minimum is obtained only when we measure the heat conduction of a double layer of fused-solid substance.

SUMMARY

1. Using an apparatus developed on the principle of a relative method, we have measured the heat conduction of 2,4,6-trinitrotoluene in the temperature range from 10-96°, i.e., in the solid and liquid states.

2. The values for the heat conduction of trotyl in the solid state agree well with the results of Belyaev and Prentiss, but differ sharply from those of Read and Lloyd, which are certainly low.

3. A sharp fall in heat conduction in trotyl in the solid state near the melting region was not observed.

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NEUTRONOGRAPHIC STUDY OF CARBIDES AND NITRIDES OF TITANIUM

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Chemical compounds of carbon and nitrogen with metals of the transitional groups have an obviously metallic character and do not obey the laws of chemical valence. Numerous attempts to establish the character of the interatomic bonds in carbides and nitrides of the transitional metals have been based chiefly on the results of x-ray investigations [1]. However, the x-ray data suffer from the deficiency that they are not very sensitive to the position of the nonmetallic elements in the elementary lattice. The arrangement of these atoms is usually based on data about the symmetry of the elementary lattice for metallic atoms, and on crystallochemical considerations [2].

Experimental and Calculated Values for Intensity of Reflections for Carbides and Nitride of Titanium

Titanium nitride, a=4.210A			Titanium carbide, a = 4.262A			Titanium carbide, a = 4.318A		
hkl	I_{exp}	I_{calc} for comp. $Ti_{0.85}N$	*hkl*	I_{exp}	I_{calc} for comp. $TiC_{0.25}$	*hkl*	I_{exp}	I_{calc} for comp. TiC
111	100	100	111	100	100	111	100	100
200	14	14	200	13	9	200	6	4
220	11	15	220	9	9	220	6	4
311	90	81	311	86	86	311	90	95
222	6	7				222	0	2
400	2	4				400	0	1
331	59	56				331	56	54
420	3	13						
422	4	12						
511	47	43						
440	1	5						
531	67	75						

The neutronographic method for studying the structures of these compounds permits correction of the x-ray data. In studying the structures of the carbides and nitrides of titanium by the neutronographic method, there are actual advantages over the x-ray method. These lie in the fact that the amplitudes of the coherent scattering of neutrons in this case are not only of the same order of magnitude, but are opposite in sign: $b_{Ti} = -0.38 \cdot 10^{-12}$; $b_C = 0.66 \cdot 10^{-12}$; $b_N = 0.94 \cdot 10^{-12}$ [3].

In [4] there was a neutronogram of titanium carbide, but it could not be used for calculation, since the authors of [4] did not give the content of carbon in the carbide which they studied. They also did not give the values for the parameters of the crystal lattice, from the values for which we could estimate the content of carbon in the carbide from the curve of relation of the lattice parameters to carbon content [5]. Therefore, we have undertaken a neutronographic study of a titanium carbide with the following values for the lattice parameters*: a = 4.262A (about 25 at. % C), a = 4.318A (about 50 at.% C), and of a titanium nitride with a = 4.210A.

*The parameters for the crystal lattices of the carbide and nitride of titanium were determined by the x-ray method of reverse exposure.

EXPERIMENTAL

We studied the composition of titanium carbide as found at the beginning and end of the region of homogeneity of this compound [1,5]. The neutronogram was obtained on a neutron diffractometer with a remote control [6]. The diffractometer was set up in one of the horizontal passages of reactor IRT-1000 of the Institute for Atomic Energy of the Academy of Sciences of the USSR [7]. The samples to be studied were put by hand in a thin-walled (0.1 mm) aluminum container with diameter 14 mm and height 30 mm. The wavelength of the neutrons, rendered monochromatic by reflection from the (111) surface of a lead crystal, was 1.06A. The neutrons scattered by the sample were recorded by a counter with BF_3, rotating at constant speed.

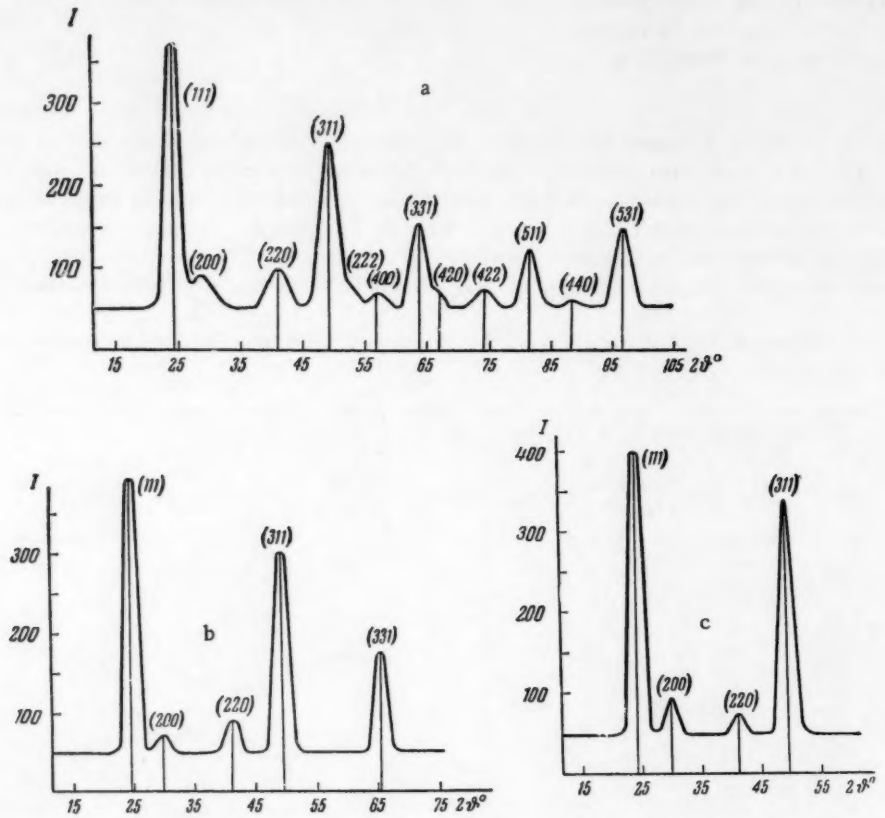

Fig. 1. Neutronograms: a) from titanium nitride with composition $Ti_{0.85}N$; b) from titanium carbide with composition $TiC_{\sim 1.0}$; c) from titanium carbide with composition $TiC_{0.25}$.

The intensity of neutron scattering was automatically recorded on a EPP-09 tape, depending on the angle of scattering. The ratio of intensities of the different reflections was determined with respect to the area under the integral curve of intensity of count, with subtraction of the base. The area was measured with a planimeter. The resulting neutronograms are given in Fig. 1.* The data on the intensity of the reflections are given in the table.

We find on the neutronograms only those reflections which satisfy the conditions of extinction of a face-centered cubic lattice. Thus, the neutronographic data confirm the x-ray evidence on the symmetry of the elementary lattice of the studied compounds. The absence on the neutronogram of superstructural reflections shows that the atoms of the nonmetal in these compounds are distributed statistically.

*Since the original neutronograms were very large, we give in Fig. 1 a reduced copy constructed from the averaged data.

Calculation for the values of the intensities was carried out by the formula [3]:

$$I_{calc.} \approx F^2 p \frac{1}{\sin^2\vartheta \cos\vartheta} A(\vartheta),$$

where F is a structural factor, p is the frequency factor; A(ϑ) is the absorption factor. The absorption factor for these compounds depends little on the angle ϑ, and so in the calculations it was not considered.

On integration of the diffraction picture there can be differences in values, because one and the same compound with different gross states, in some cases, gives the same ratio of intensities of reflection. We consider the ratio $F^2_{(111)}/F^2_{(200)}$ for carbide and nitride of titanium; let

$$F^2_{(111)}/F^2_{(200)} = \frac{(zb_{Ti} - b_N)^2}{(zb_{Ti} + b_N)^2} = A,$$

where z is the ratio of content of titanium and nonmetal in the compound; b_{Ti} and b_N are the amplitude of scattering by titanium and nonmetal, respectively, and A is the experimental ratio of intensities. It is easy to see that

$$z = \frac{(1 + A) + 2\sqrt{A}}{u(1 - A)},$$

where $u = b_{Ti}/b_N$.

For the study of titanium nitride, the experimental value A is 4.1. In this case, $z_1 = 7.2$ and $z_2 = 0.85$. The composition of the titanium nitride can be written in the form $Ti_{0.85}N$ and $Ti_{7.2}N$. However, the latter composition should have a hexagonal lattice as a solution of nitrogen in titanium. Hence, in studying titanium nitride, the titanium atoms do not occupy all the vacant places in the lattice of metallic atoms. The somewhat greater hemisphere of reflections for titanium nitride, as compared to the reflection from titanium carbide, is connected with the defectiveness of the lattice. There is other evidence for a defective lattice in titanium nitride [8]. However, the lack of titanium found by measuring the density (about 4%) is somewhat lower than we find. For titanium carbide the experimental value A at a composition close to the stoichiometric is 14. Here, $z_1 = 3$ and $z_2 = 1$, i.e., the possible compositions are TiC , $TiC_{0.33}$ (or Ti_3C). The latter composition drops out, since, on the basis of x-ray evidence, this preparation contains about 50 at.% C, i.e, its formula is TiC.

SUMMARY

1. Neutronographic data show that in titanium carbide $TiC_{0.25}$, and in compositions close to the stoichiometric, the titanium atoms occupy all possible vacant places. The calculated intensity values for titanium carbide with composition TiC and $TiC_{0.25}$, and for titanium nitride with composition $Ti_{0.85}N$ agree well with the experimental values.

2. In titanium carbide and nitride the atoms of the nonmetal actually occur in octahedral spaces. In titanium carbide with insufficient carbon the octahedral spaces are occupied statistically. In titanium nitride the lattice is defective with respect to titanium.

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THE REACTIONS OF ALKENYL- AND ALKYLGERMANIUM CHLORIDES WITH HYDROGEN BROMIDE

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Among the general methods for preparing alkylgermanium bromides, almost the most suitable is that of treating the corresponding organogermanium oxides with hydrobromic acid [1-3]:

$$Cl_nGeR_{4-n} \xrightarrow{H_2O} [\text{oxide}] \xrightarrow{40\%\,HBr} Br_nGeR_{4-n}.$$

Another prevalent method consists in splitting Ge–C, Ge–H, and Ge–Ge bonds with bromine or hydrogen bromide, sometimes in the presence of aluminum bromide [1,4-6]:

$$R_4Ge \xrightarrow{Br_2} R_3GeBr \xrightarrow[AlBr_3]{Br_2} R_2GeBr_2.$$

Alkylgermanium bromides are also formed in a "direct synthesis" using alkyl bromides [7-9]:

$$RBr \xrightarrow[400^\circ]{Ge\text{-}Cu} R_2GeBr_2 + RGeBr_3.$$

There is often mention, also, in the literature, of formation of alkylgermanium bromides by partial alkylation with a Grignard reagent not only of $GeBr_4$, but also of $GeCl_4$ or alkyl (aryl) germanium chlorides [8-10]:

$$GeCl_4 + RMgBr \rightarrow [R_nGeCl_{4-n}] \xrightarrow{MgBrCl} R_nGeBr_{4-n} + MgCl_2.$$

Replacement of chlorine by bromine on a silicon atom in the analogous reaction in the organic silicon compounds is encountered very rarely, probably because of the lower degree of ionization of the Si–Cl bond as compared to the Ge–Cl bond.

In attempting to add HBr to allyltrichlorogermanium, we unexpectedly found quantitative formation of allyltribromogermanium:

$$Cl_3GeCH_2CH = CH_2 + 3HBr \rightarrow Br_3GeCH_2CH = CH_2 + 3HCl.$$

Heating and use of benzoyl peroxide in this reaction (with long bubbling in of HBr) did not change the result, that is, allyltribromogermanium did not add hydrogen bromide either. Analogous results were obtained with vinyltrichlorogermanium:

$$Cl_3GeCH = CH_2 \xrightarrow{HBr} Br_3GeCH = CH_2.$$

At the same time, it is known that HBr adds to allyltrichlorosilane exclusively at the multiple bond [11]:

$$Cl_3SiCH_2CH = CH_2 + HBr \rightarrow Cl_3SiCH_2CH_2CH_2Br.$$

Only in the case of methylallyltrichlorogermanium, besides replacement of the chlorine atoms on the germanium by bromine, is there addition of HBr at the double bond:

$$Cl_3Ge - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2 \xrightarrow{HBr} Br_3GeCH_2C(Br)(CH_3)_2.$$

Starting compound	Organogermanium bromide	Yield, %	B.p., °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.
$GeCl_4$	$GeBr_4$	83	180—181 (756)	1,6230	3,0845	44,84	44,40
n-$C_4H_9GeCl_3$	n-$C_4H_9GeBr_3$	96	90 (9)	1,5606	2,1486	55,66	55,32
$CH_2=CHGeCl_3$	$CH_2=CHGeBr_3$	73	55 (7)	1,5883	2,5420	45,338	45,548
$CH_2=CHCH_2GeCl_3$	$CH_2=CHCH_2GeBr_3$	98	56 (2)	1,5874	2,3274	51,07	50,196
$CH_2=CCH_2GeCl_3$ | CH_3	$(CH_3)_2CCH_2GeBr_3$ | Br	62	123—128 (8)	1,5920	2,3822	63,67	63,04
$(C_2H_5)_2GeCl_2$	$(C_2H_5)_2GeBr_2$	89	82—86(16)	1,5359	1,9854	45,62	47,65
$(C_2H_5)_3GeCl$	$(C_2H_5)_3GeBr$	80	68 (10)	1,4836	1,4009	48,91	49,35

Note: All the compounds given in the table were determined by alkali titration [12] of the theoretical amount of bromine.

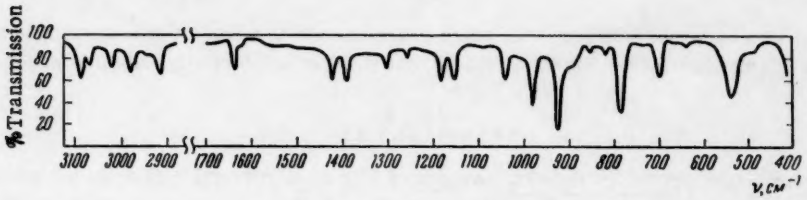

Fig. 1. Infrared spectrum of $CH_2 = CHCH_2GeBr_3$.

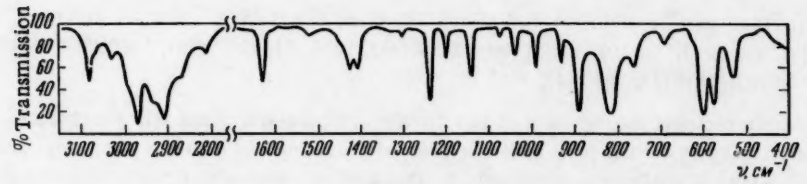

Fig. 2. Infrared spectrum of $CH_2 = CHCH_2Ge(CH_3)_3$.

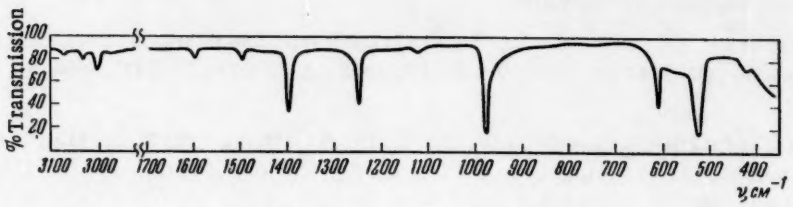

Fig. 3. Infrared spectrum of $CH_2 = CHGeBr_3$.

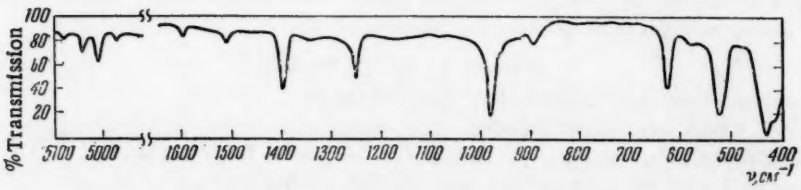

Fig. 4. Infrared spectrum of $CH_2 = CHGeCl_3$.

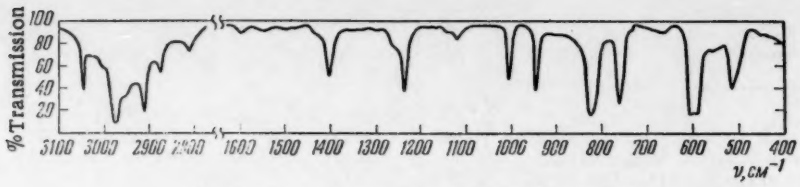

Fig. 5. Infrared spectrum of $CH_2 = CHGe(CH_3)_3$.

Further study showed that this reaction has a general character and can serve as a very convenient method for the synthesis not only of various alkenyl, but also alkylgermanium bromides, formed according to the equation

$$R_{4-n}GeCl_n + n \cdot HBr \rightarrow R_{4-n}GeBr_n + n \cdot HCl,$$

where n = 1, 2, 3, and 4.

Such a reaction with hydrogen bromide is not found in the chemistry of organic silicon compounds. We also obtained allyltribromogermanium by the "direct method," that is, by reaction of allyl bromide with germanium–copper powder.

EXPERIMENTAL

Allyltribromogermanium $CH_2 = CHCH_2GeBr_3$. We passed 95 g of allyl bromide (2 drops per min) through a glass tube (length 230 mm, diameter 18 mm) filled with a mixture of finely broken up germanium (20 g) and copper (5 g) heated to 300 ± 10° in a stream of nitrogen. We isolated from the resulting condensate 47 g of allyl bromide and 34 g of allyltribromogermanium with b.p. 72° (7 mm), $n^{20}D$ 1.5882; d^{20}_4 2.3410; found MR 50.82; calculated MR 50.20.

Infrared spectrum ($\Delta\nu$, cm^{-1}): 155 (5w), 235 (10w), 269 (8w), 312 (6v.w.), 325 (5w), 403 (1w), 534 (7v.w.), 696 (9w), 786 (0), 930 (5w), 991 (0), 1152 (10w), 1184 (4n), 1245 (1), 1297 (7n), 1388 (7w), 1417 (5n), 1633 (10n), 2915 (7w), 2955 (4), 3013 (4), 3085 (4).

We bubbled hydrogen bromide through 36 g of allyltrichlorogermanium. After 5 hr we obtained the theoretical weight, which was not changed by further passing of HBr even with heating and addition of benzoyl peroxide. Vacuum distillation gave 52.5 g of allyltribromogermanium, methylation of which with CH_3MgCl gave a yield of 90% of allyltrimethyl germanium. The spectrum of the latter agreed completely with a standard. The remaining experiments were carried out in an analogous way (see table). Below we give the spectra of some germanium compounds, obtained by L. A. Leites, for which we thank him.

Infrared spectrum of $CH_2 = CHGeBr_3$ ($\Delta\nu$, cm^{-1}): 183 (1), 234 (4n), 256 (10w), 301 (7w), 328 (1), 351 (2w), 525 (1), 604 (7w), 994 (1), 1240 (8), 1389 (8), 1422 (1), 1596 (5), 2856 (1), 2954 (2), 2996 (8), 3026 (3), 3071 (5).

Infrared spectrum of $CH_3CH_2CH_2CH_2GeBr_3$: ($\Delta\nu$, cm^{-1}): 152 (2), 175 (0), 216 (7), 247 (10), 284 (2), 308 (4w), 328 (2w), 506 (0), 548 (1), 631 (5), 659 (2), 981 (0), 1007 (0), 1043 (1), 1092 (1), 1149 (3), 1181 (1), 1200 (5w), 1346 (0), 1448 (1w).

SUMMARY

We present a new method for the synthesis of organic germanium bromides which consists in bubbling hydrogen bromide through the corresponding organic germanium chlorides.

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A NEW METHOD FOR THE SYNTHESIS OF MACROCYCLIC KETONES

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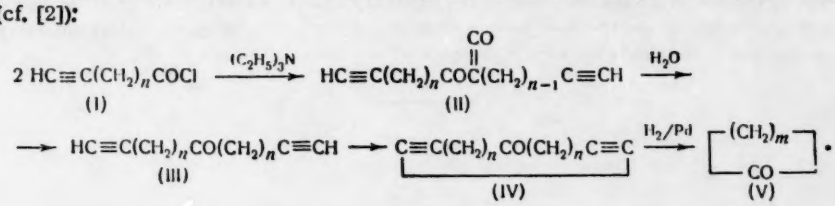
Original article submitted May 29, 1961

We recently described a method for the synthesis of macrocyclic unsaturated lactones, based on the oxidative condensation of ω,ω'-diacetylene esters [1]. Now we have extended this cyclization process to ω,ω'-diacetylene ketones (III) which we have synthesized from ω-acetylene acid chlorides (I) through the corresponding ω,ω'-diacetylene ketenes (II) (cf. [2]):



By the action of triethylamine in ether solution with later hydrolysis of the nonynonyl chloride (I, n = 6) and undecynonyl chloride (I, n = 8), they were converted into 1,6-heptadecadiyn-9-one [(III, n = 6) and 1,20-heneicosadiyn-11-one (III, n = 8)]. Oxidative condensation of these ketones under conditions of high dilution [1] led to satisfactory yields of diacetylene macrocyclic ketones 8,10-cycloheptadecadiyn-1-one (IV, n = 6) and 10,12-cycloheneicosadiyn-1-one (IV, n = 8), which represent a new type of macrocyclic compound. The diacetylene ketones are thick, colorless oils characterized as the corresponding dinitrophenylhydrazones; their individuality was shown chromatographically on paper and by thin-layer chromatography on aluminum oxide (see Experimental). The structure of the diacetylene macrocyclic ketones (IV) was confirmed by ultraviolet spectra (presence of bands characteristic for conjugated diacetylenes at 227, 238, and 254 mμ [3]). By catalytic hydrogenation of these ketones they were converted to the known saturated macrocyclic ketones cycloheptadecanone (V, m = 16 [4]) and cycloheneicosanone (V, m = 20 [5,6]). The infrared spectrum of the seventeen-membered diacetylene macrocyclic ketone (IV, n = 6) taken in carbon tetrachloride or in vaseline oil, contains the normal bands for a ketonic CO group, while in the infrared spectrum of the analogous seventeen-membered lactone (10,12-hexadecadiyn-1,16-olide) taken in vaseline oil, the band of the lactone CO group is shifted toward lower frequencies [1]. In distinction from the saturated ketones (V) which have a weak musk odor, the diacetylene ketones (IV) practically lack an odor.

EXPERIMENTAL

ω,ω'-Diacetylene ketones (III). To a solution of 8.92 g of 8-nonynonyl chloride [1] in 100 ml of dry ether cooled to 5° was added, in the course of 10 min with intensive stirring, 5.72 g of triethylamine. Stirring was continued for 1 hr at 5°, then for 12 hr at room temperature and for 1 hr in the boiling mixture. After the latter had been cooled, it was washed with 2% sulfuric acid and water. The ether solution was evaporated in a vacuum and the residue was heated for 1 hr on a water bath, stirring with 100 ml of 2% KOH solution. The mixture was cooled with ice, the crystals were separated and twice recrystallized from a mixture of methanol–acetone (4:1). We obtained 3.5 g (55%) of 1,16-heptadecadiyn-9-one (III, n = 6), colorless prisms with m.p. 31-32°. The infrared spectrum in vaseline

We have been able to show that on heating (2-3 hr at 100°) ethyl esters of α-amino acids in a sealed tube with ethylene sulfide, they undergo N-β-mercaptoethylation, forming good yields of the corresponding aminomercaptans. For example, we have thus prepared the ethyl ester of N-(β-mercaptoethyl)glycine (b.p. 74-74.5°, 2 mm, $n^{20}D$ 1.4912; d^{20}_4 1.1252; MR 42.03. $C_6H_{13}O_2NS$. Found: MR 42.81; literature data [3], b.p. 116-118°, 4 mm), and the ethyl ester of N-(β-mercaptoethyl)-α-alanine (b.p. 75-75.5°/1.5 mm, $n^{25}D$ 1.4671; d^{25}_4 1.0402; MR 47.28. $C_7H_{15}O_2NS$. Found: MR 47.43; not described in the literature).

Study of the reaction of N-β-mercaptoethylation of natural and synthetic amino acids will be continued; later we will publish the details of the synthesis and some of the physical and chemical properties and reactions of this new class of compounds, and also data on their possible use and that of their chemical transformation products in biological experiments.

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3. E. Felder, F. Bonati, and S. Bianchi, Experientia 15, 32 (1959).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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oil, ν_{max} 1719 (s), 2110 (m), 3318 (s) cm^{-1}; in CCl_4, 1719 (s) cm^{-1}. Found: C 82.40; H 10.65%. $C_{17}H_{26}O$. Calculated: C 82.87; H 10.64%.

In an analogous way we obtained from 10-undecynoyl chloride [1] 25% of 1,20-heneicosadiyn-11-one (III, n = 8), m.p. 46-47° (from a mixture of methanol–acetone 4:1). Infrared spectrum in vaseline oil ν_{max} 1706 (s), 2112 (w), 3300 (s) cm^{-1}. Found: C 82.92; H 11.20%. $C_{21}H_{34}O$. Calculated: C 83.38; H 11.33%.

Diacetylene macrocyclic ketones (IV). A solution of 2.8 g of 1,16-heptadecadiyn-9-one in 10 ml of ether was added through a nozzle for high dilution [7] in the course of 5 hr with energetic stirring to a boiling solution (84-86°) of 10 g of anhydrous copper acetate in 1.5 liters of a mixture of pyridine–ether (5:1). After cooling, the mixture was filtered through 500 g of aluminum oxide (activity II) which was then washed with 1 liter of ether. The filtrate was evaporated in a vacuum to a volume of 60-70 ml, diluted with 300 ml of ether and poured into 1 liter of 1 N hydrochloric acid with ice; the ether layer was separated, the water solution was extracted with ether (3 × 100 ml), the combined extracts were washed with water, dried with magnesium sulfate, and the ether was distilled off. The residue was dissolved in petroleum ether (b.p. 40-60°) and passed through 30 g of aluminum oxide (activity II) and then this was washed with 200 ml of petroleum ether. The residue obtained after distillation of the solvent was chromatographed in ether on a column (16 × 150 mm) with activated charcoal. The first portion of the eluate (4 × 50 ml) contained pure 8,10-cycloheptadecadiyn-1-one (IV, n = 6)*; yield 1.55 g (56%) of colorless oil with R_f 0.825 (paper "B," methanol). Infrared spectrum in vaseline oil: ν_{max} 1716 (s), 2154 (w), 2251 (w) cm^{-1}; in CCl_4, 1720 (s) cm^{-1}. Ultraviolet spectrum (in ethanol) λ_{max} 226.5, 237.5, 254.5 mμ; (ϵ 379, 311, 148). Found: C 83.59; H 10.25%. $C_{17}H_{24}O$. Calculated: C 83.53; H 9.90%.

2,4-Dinitrophenylhydrazone of 8,10-cycloheptadecadiyn-1-one, recrystallized from alcohol, had m.p. 95-96° with decomposition. Found: N 13.12%. $C_{23}H_{28}N_4O_4$. Calculated: N 13.20%.

Under the same conditions, from 3.58 g of 1,20-heneicosadiyn-11-one we obtained 2.13 g (60%) of 10,12-cycloheneicosadiyn-1-one (IV, n = 8) in the form of a colorless oil with R_f 0.867 (paper "B," methanol). Infrared spectrum in vaseline oil: ν_{max} 1715 (s). Ultraviolet spectrum (in alcohol): λ_{max} 227, 240, 254 mμ (ϵ 553, 518, 378). Found: C 83.69; H 10.72%. $C_{21}H_{32}O$. Calculated: C 83.93; H 10.73%. 2,4-Dinitrophenylhydrazone melted with decomposition at 69-70° (from alcohol). Found: N 11.74%. $C_{27}H_{36}N_4O_4$. Calculated: N 11.66%.

Saturated macrocyclic ketones (V). We hydrogenated 0.126 g of 8,10-cycloheptadecadiyn-1-one over 0.02 g of 5% Pd/$CaCO_3$ in 10 ml of alcohol until absorption of hydrogen stopped (45 ml); then we filtered, evaporated, and chromatographed the residue in n-heptane on a column (12 × 160 mm) with aluminum oxide (activity II); and eluted with a mixture (4 × 50 ml) of n-heptane–benzene, 9:1. We obtained cycloheptadecanone (V, m = 16) [4] with m.p. 62.5-64°; 2,4-dinitrophenylhydrazone, m.p. 85.5-86° (from alcohol). Found: N 12.99%. $C_{23}H_{36}O_4N_4$. Calculated: N 12.95%.

In an analogous way we reduced 10,12-cycloheneicosadiyn-1-one to cycloheneicosanone (V, m = 20) [5,6], m.p. 46-48° (from alcohol); 2,4-dinitrophenylhydrazone with m.p. 53-54° (from alcohol). Found: 11.14%. $C_{27}H_{44}O_4N_4$. Calculated: N 11.46%.

SUMMARY

We have described the synthesis of macrocyclic diacetylene ketones by oxidative condensation of aliphatic ω,ω'-diacetylene ketones.

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*The individuality of the substance in the eluate was controlled by chromatography on a plate with aluminum oxide (activity II) in a mixture of n-heptane–benzene–ether (10:1:1). It was developed with a 1% solution of potassium permanganate in 2 N H_2SO_4.

LETTERS TO THE EDITOR

A NEW METHOD FOR PREPARING STEREOSPECIFIC SILICA GELS

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
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Original article submitted June 14, 1961

Stereospecific silica gels can be prepared as a result of the hydrolysis of optically active derivatives of orthosilicic acid. The synthesis of optically active tetraalkoxysilanes was carried out by reaction (80°) for 5 hr of 0.028 M of an optically active hydroxyl-containing compound with 0.027 M of $SiCl_4$ in 0.11 M pyridine with 50 ml of benzene. The precipitate was filtered off, the filtrate was distilled in a vacuum, and the product was purified by crystallization or fractionation. We obtained tetra-(2-methylbutoxy)silane (I); b.p. 153-154° (7 mm), $n^{20}D$ 1.4105, d^{20}_4 0.8892; $[\alpha]^{20}_4 = +1.27°$ (initial 2-methylbutanol: $[\alpha]^{20}D = -25.2°$); tetramenthoxysilane; b.p. 256-258° (1 mm), m.p. 97.8-98.0°, $[\alpha]^{20}D = -89.7°$; tetrabornyloxysilane, m.p. 290-291°, $[\alpha]^{20}D = -37.8°$. The alkoxysilane obtained by reaction of di-n-butyltartrate ($[\alpha]^{20}D = +10.7°$) with $SiCl_4$ was hydrolyzed without isolation. Hydrolysis of the tetraalkoxysilanes was carried out at 40° in dioxane with 2 M water and 0.05 M HCl. The silica gel was filtered off, dried in a stream of air with 60% humidity, and was extracted with methanol to a moisture content of 18%. Data were obtained on the stereospecific adsorption of optical isomers on these silica gels. Thus, on adsorption by the weight method on the silica gel from (I) of the racemate and the (+) and (-) isomers of 2-butanol, it was found that the total amounts of alcohol adsorbed by saturation at 0° was 4.16, 3.36, and 3.94 mM/g, respectively.

EXCHANGE REACTIONS BETWEEN ESTERS OF BORIC AND BOROORGANIC ACIDS AND THEIR THIOANALOGS

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
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Original article submitted September 26, 1961

Long study of the exchange reactions between various types of organic compounds of boron has shown us that esters of boric, alkyl-, or dialkylboric acids react with each other, exchanging the alkoxyl groups. The esters of the above-mentioned acids undergo an analogous reaction with esters of thioboric, alkyl-, or dialkylthioboric acids. The equilibrium reactions expressed by the following equations occur slowly at room temperature and rapidly with heating:

$$3RB(OR')_2 + 2(R''O)_3B \rightleftarrows 3RB(OR'')_2 + 2(R'O)_3B$$

$$3RB(OR')_2 + 2(R''S)_3B \rightleftarrows 3RB(SR'')_2 + 2(R'O)_3B$$

$$RB(OR')_2 + R'''B(SR'')_2 \rightleftarrows RB(SR'')_2 + R'''B(OR')_2$$

$$3R_2BOR' + (R''S)_3B \rightleftarrows 3R_2BSR'' + (R'O)_3B$$

$$2R_2BOR' + R'''B(SR'')_2 \rightleftarrows 2R_2BSR'' + R'''B(OR')_2$$

$$R_2BOR' + R'''_2BSR'' \rightleftarrows R_2BSR'' + R'''_2BOR'.$$

If by distillation we remove the most volatile component from the reaction mixture, the equilibrium is completely shifted to the side of its formation. Thus, starting from compounds which contain in the ester group radicals of different molecular weights, it is possible to carry out a transfer from the ester of the oxygen acid to its thioanalog, and the reverse, which is important from the standpoint of method.

Such exchange reactions also occur with amino derivatives of boron. Thus, for example, heating an ester of alkylboric acid with dialkyl-(phenylamino)boron with distillation of the ester of dialkylboric acid gives N-phenyl-substituted alkyl-(amino)boron.

THE SYNTHESIS OF 3,3,3-TRICHLORO-1-PROPENE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
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Original article submitted October 6, 1961

In the journal "Industrial and Engineering Chemistry" for 1961, was published a letter of Ladd and Towney [1], in which they objected to Skinner [2] assigning us priority in obtaining 3,3,3-trichloro-1-propene, and asserting that Ladd and Shinkle had obtained this substance previously.

In this connection, we wish to make the following statement: In a series of our publications devoted to the chemistry of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes and related compounds, we reported a method for preparation, chemical and physical properties, of 3,3,3-trichloro-1-propene. The first paper relating to this question was received by the editor of "Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk" on November 2, 1950, and was published in May, 1951 [3], i.e., earlier than the claim of Ladd and Shinkle [4].

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N-β-MERCAPTOETHYLATION OF AMINO ACID ESTERS

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The reaction of N-β-mercaptoethylation of aromatic and aliphatic amines by ethylene sulfide is well known and described in the literature [1,2]. We have considered it important for biological investigations to prepare N-(β-mercaptoethyl)amino acids and their derivatives; the sole example of the synthesis of such a compound has been described only recently [3]: the synthesis of the ethyl ester of N-(β-mercaptoethyl)glycine was carried out through the corresponding N-ethyleneimino derivative.

We have been able to show that on heating (2-3 hours at 100°) ethyl esters of α-amino acids in a sealed tube with ethylene sulfide, they undergo N-β-mercaptoethylation, forming good yields of the corresponding amino-mercaptans. For example, we have thus prepared the ethyl ester of N-(β-mercaptoethyl)glycine (b.p. 74-74.5°C, 2 mm, n_D^{20} 1.4912; d_4^{20} 1.1252; MR 42.03. $C_6H_{13}O_2NS$. Found: MR 42.81; literature data [3], b.p. 116-118°/4 mm), and the ethyl ester of N-(β-mercaptoethyl)-α-alanine (b.p. 75-75.5°/1.5 mm, n_D^{25} 1.4671; d_4^{25} 1.0402; MR 47.28. $C_7H_{15}O_2NS$; Found: MR 47.43, not described in the literature).

Study of the reaction of N-β-mercaptoethylation of natural and synthetic amino acids will be continued; later we will publish the details of the synthesis and some of the physical and chemical properties and reactions of this new class of compounds, and also data on their possible use and that of their chemical transformation products in biological experiments.

LITERATURE CITED

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Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Life Sciences: Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Life Sciences: Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Life Sciences: Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences: Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
		Mathematics: Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics: Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Physics: Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (In English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48 1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4 1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1 1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1 1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1 1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i teoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.- Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. —Publisher.